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LXXXIII. *The Excitation of Characteristic X-rays from certain Metals.* By FRANK HORTON, *Sc.D., F.R.S.*,
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*D.Sc.**

THE well-known researches of Moseley established the fact that the characteristic X-ray spectra of the elements change in an orderly manner as we pass from element to element down the Periodic Table. This regularity has received theoretical explanation on the basis of Bohr's theory of atomic structure, according to which the X-ray spectra arise from the removal of an electron from one of the inner electronic groups of the atom and the subsequent readjustment of the remaining electrons of the system. Thus the K series of characteristic emission lines arises from the displacement of an electron from the innermost group, which, according to the theory, is complete in the helium atom and remains unaltered throughout the elements of higher atomic number. The binding of the two electrons in this group in any atom depends on the nuclear charge, but is practically independent of the presence of electrons in the groups of higher quantum number.

In the process of atom building the L, M, etc., electronic groups do not attain completion until elements of higher atomic numbers are reached (*e. g.*, the L group until neon for which $z=10$); but after each group is completed in turn, the binding to the nucleus of the electrons in this group is

* Communicated by the Authors.

influenced mainly by the increasing charge on the nucleus, as we pass from element to element, and only to a secondary extent by the electrons which gradually fill up the outer groups. The existence of the Moseley relation between the atomic numbers of the elements and the frequency of any particular X-ray emission line (or absorption limit) of those elements, is attributed to this persistence of the inner groups unchanged throughout the elements of atomic numbers higher than those at which each group is complete. In accordance with theory, it would be expected that in passing down the Periodic Table the Moseley relation for any given set of lines (or absorption limits) would cease to hold at the element at which a change occurs in the constitution of the particular electronic group to which the set of lines is due. On Bohr's view of the process of the binding of the electrons to the nucleus, the M group changes between the elements calcium ($z=20$) and copper ($z=29$) from a system containing two sub-groups of four electrons each to a system containing three sub-groups of six electrons each. The energy required to remove an electron from any one of these sub-groups corresponds to one of the M X-ray absorption limits. Experimental evidence suggests that the third M sub-group of electrons commences at scandium ($z=21$), and that the development of the M shell to three sub-groups of six electrons each is for the first time complete at copper ($z=29$), but so far as the authors are aware, no details have been published of the constitution of the M group in the elements of atomic numbers between 22 and 29. It seemed possible that evidence bearing on this point might be obtained from observations of the excitation potentials required to produce the characteristic M radiations of the elements with atomic numbers in and near this region.

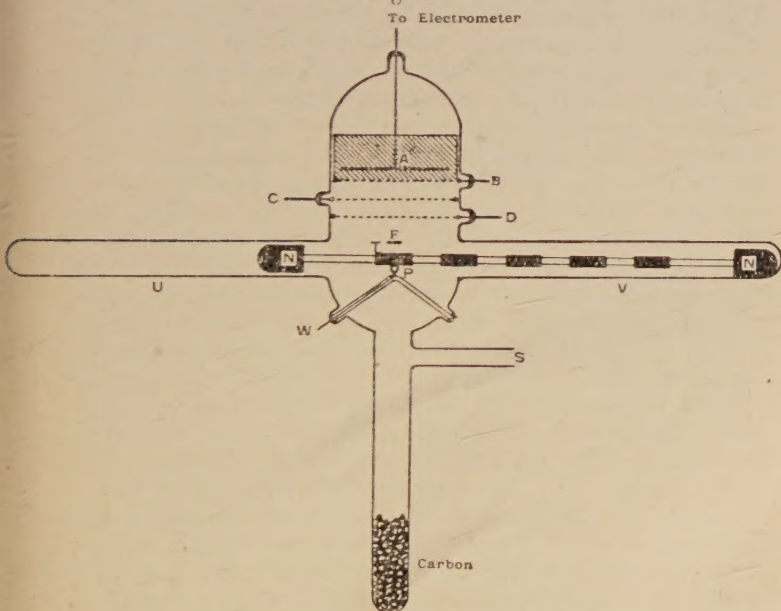
The excitation potential method of investigating X-ray absorption limits consists in measuring the photoelectric current caused by the X-radiation emitted by a given element under electronic bombardment with gradually increasing energy of the electron stream, and in determining, from the positions of discontinuities in the current-potential curves, the critical points at which new radiations are produced. This method of experimenting is particularly valuable for investigations in that part of the spectrum between the longest wave-length measurable with an X-ray spectrometer and the shortest wave-length measurable with a vacuum grating spectroscope, an interval which is at present about three octaves.

The present paper records the results of observations by this method on the elements iron, nickel, copper, and zinc, which fall within the region of atomic numbers referred to. The excitation potentials for aluminium have also been investigated, and the results are included. Investigations by this method, of the potentials of excitation of characteristic X-radiations from some of these elements, have recently been published by Kurth* and by Mohler and Foote†, and their results will be referred to in the course of the paper.

Apparatus and Method.

It is essential for the success of the experiments that the electronic bombardment of the element under test should be

Fig. 1.



carried out in a vacuum as nearly perfect as it is possible to obtain. The glass vessel in which the electrodes were contained was therefore constructed without any waxed or cemented joins. It had a tube (see fig. 1) 2 cm. wide, containing charcoal which was cooled in liquid air during the observations, and it was connected by a side tube S, through

* E. H. Kurth, *Phys. Rev.* xviii. p. 461 (1921).

† F. L. Mohler and P. D. Foote, *Sci. Papers, Bur. of Standards*, No. 425.

a wide bore stop-cock and a U-tube immersed in liquid air, with a diffusion pump which was maintained in operation throughout the measurements. Before beginning the observations, the apparatus was pumped out and the residual gas removed as completely as possible from the filaments, electrodes, and glass walls of the apparatus by long-continued heating in an air oven and simultaneous pumping with the diffusion pump.

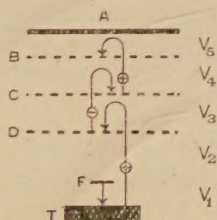
The metals which formed the targets for the electron bombardment were supplied as pure by Messrs. Johnson, Matthey & Co. They were arranged in a row on two parallel thin quartz rods which ran through holes drilled in them. Each target was 2 cm. \times 1 cm. \times 0.5 cm., and they were kept apart by pieces of quartz tubing 1.5 cm. long which fitted over the rods in the spaces between the metals. The extreme ends of the quartz rods fitted into two pieces of soft iron as indicated in the figure (N, N), so that by means of electromagnets the whole row could be moved along the horizontal tube U, V, and each target in turn could be placed underneath the tungsten filaments F which supplied the bombarding electron stream. An electrical connexion to the particular element under examination was made by means of the platinum wire W, at the upper end of which was a small platinum ball P, which pressed against the lower face of the target. This arrangement has the great advantage that the element under investigation can be quickly changed so that each element can be examined in turn, and it can be rapidly ascertained whether an indication of a critical point in a current-voltage curve is a genuine effect due to the element, or whether it arises from some other cause, in which case it would be common to the whole series of curves. The row of targets could be turned over in the apparatus by means of an electromagnet so that the arrangement permitted of the use, in turn, of both faces and both edges of each target. Thus a considerable surface of each was available for bombardment, and the part in use could be changed as soon as it showed signs of being contaminated by the sputtering of the glowing filaments. In the actual apparatus, the tubes U and V were rather longer than they are represented as being in the figure. This allowed of the whole row of targets being moved into one or other of these tubes during the preliminary heating of the filaments in the process of ridding them of occluded gases, so that the surface of the targets was not contaminated during this process.

The apparatus contained two V-shaped tungsten filaments,

each about 1.5 cm. long in the glowing portion. They were introduced from opposite sides of the main glass tube, and were close together in the same horizontal plane in the position indicated by F in the figure. In most of the earlier observations only one filament was used at a time, the other being kept in reserve; but in many of the later experiments the two were used simultaneously, for it was found that the increased bombardment thus obtained made the effects sought for more marked.

The radiations stimulated by the electron bombardment of the targets were detected by means of their photoelectric effects on a platinum plate A, connected to a delicate electrometer. The platinum wire leading to A was protected by earthed guard rings from collecting charges by leakage along the inner or outer surfaces of the glass tube through which it was sealed. A hangs inside a short hollow platinum cylinder, the base of which is of fine platinum gauze B. C and D are two circular pieces of fine platinum gauze which fill the horizontal section of the central tube of the apparatus, as indicated in the diagram. B, C, and D are about 8 mm. apart, while D is about 13 mm. above the filaments. This arrangement of the plate A and of the three platinum grids is similar to that which has been employed by Horton and Davies in their measurements of the critical potentials for the production of radiation from gases. By suitably selecting the values of the electric fields between these grids it is possible to arrange that the electrometer is only deflected by radiation illuminating the plate A

Fig. 2.



or the surrounding platinum cylinder. An arrangement of electric fields which secures this result is indicated diagrammatically in fig. 2. Electrons from the filament F bombard the target T with energy due to a fall through a potential difference V_1 which could be increased up to 230 volts. The lower gauze D was maintained at V_2 volts negative to the filament; C was V_3 volts positive to D, V_3 being always

greater than $V_1 + V_2$, so that none of the positive ions which are liberated by the electron bombardment of the target and which pass through the gauze D can travel to the level of C. The experiments of Horton and Davies have shown, however, that such positive ions will liberate electrons from the platinum gauze D when their velocity of impact exceeds a certain small amount (that due to a fall through about 20 volts in the case of the positive ions from platinum). Any electrons so liberated are accelerated by the field V_3 towards the collecting electrode, but are prevented from reaching that electrode by the field V_4 between the gauzes C and B. Any positive ions liberated from C under the bombardment of these electrons could be turned back by the field V_5 between the plate A and the gauze B, but experiment showed that the number of these positive ions was too small to give a detectable effect. The field V_5 was therefore usually kept at a small constant value during the observations, so as to give greater steadiness to the electrometer readings than is obtained if this field is large. By reversing the direction of V_5 , the direction of the photoelectric current between A and B is reversed, thus making it possible to verify that the current measured by the electrometer is due to photoelectric action and does not arise from some spurious ionization effect.

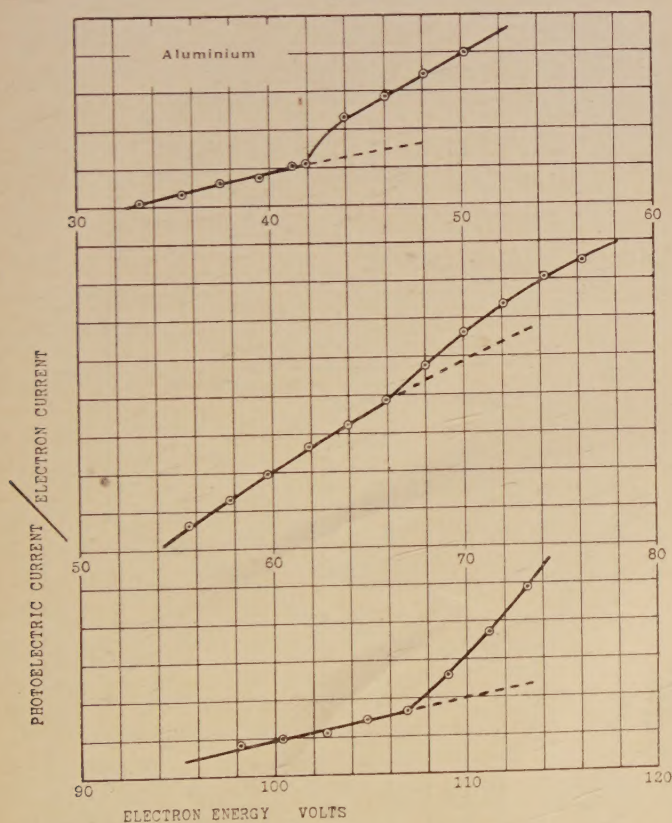
During the measurements of the photoelectric currents with the electrometer the total electron current between the filament and the target was also measured on a galvanometer. In this way a series of values of the photoelectric current per unit bombarding electron current was obtained, and these values were plotted against the corresponding values of the energy of the bombarding electrons. These values were obtained by adding to the various applied potential differences V_1 a small correction determined experimentally in the usual manner.

Experimental Results and Discussion.

Within the limits of electron energies investigated, *i. e.* up to 230 volts, definite indications of the existence of two critical values for the production of characteristic radiations were found with each of the targets, iron, nickel, copper, and zinc, while in the case of aluminium three critical values were obtained. Radiation was first detected from the targets when the energy of the electron stream was about 11 volts. Whether this first detection of radiation merely indicates the stage at which, with this apparatus, the photoelectric effect of the general impulse radiation (as distinct

from characteristic radiation) becomes measurable, or whether 11 volts correspond to the energy necessary to displace or to remove one of the most loosely attached electrons of the atomic system, is a matter requiring further investigation. Observations were first taken over ranges of about 60 volts at a time. The regions at which indications of bends in the curves were found were then investigated, and the results of some of the curves obtained over these limited ranges are given below.

Fig. 3.



Aluminium.

Curves showing the three critical voltages for this metal are given in fig. 3. The values deduced for these voltages from several sets of curves are 42, 66, and 107 volts.

Fig. 4 shows the two breaks which were located in the curves for this element, the first being at 73 volts and the second at 166 volts.

Fig. 4.

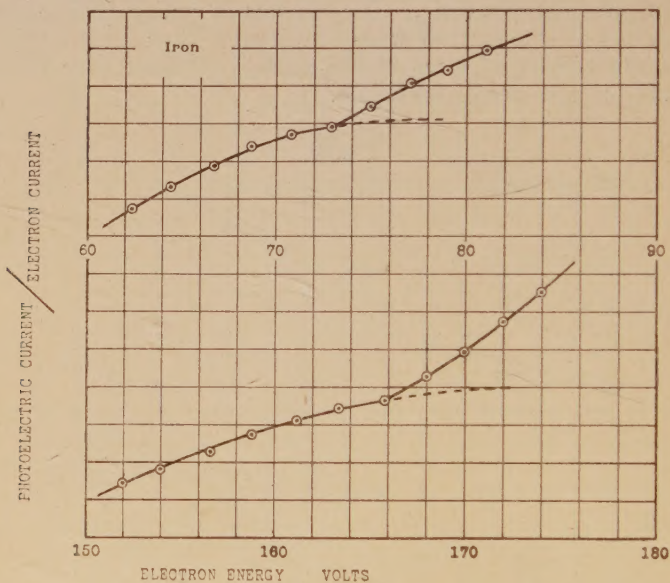
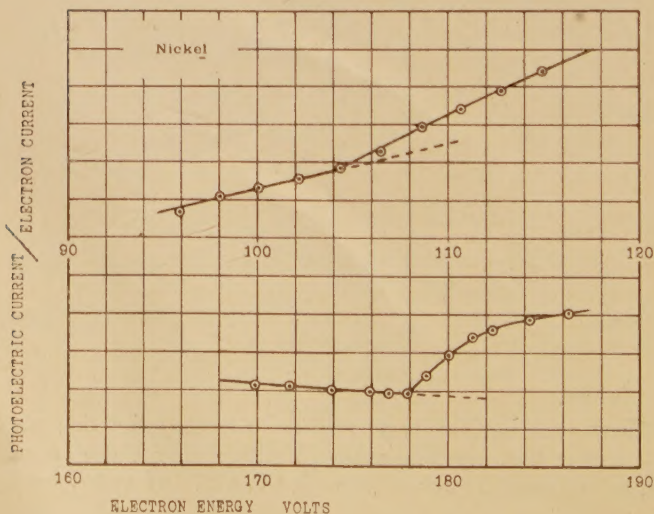


Fig. 5.



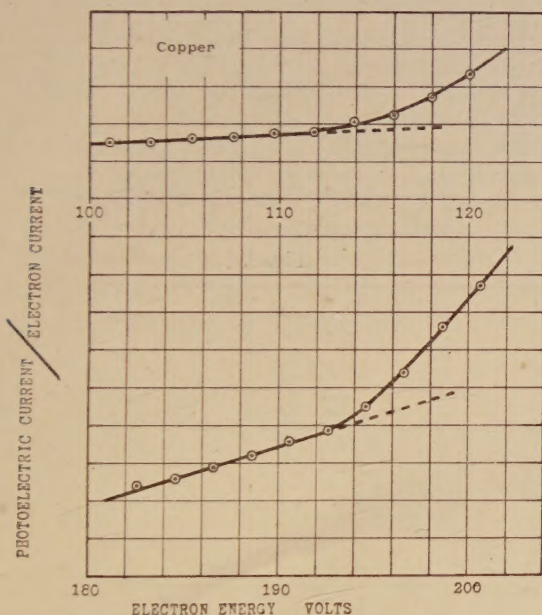
Nickel.

For this metal, as shown in fig. 5, discontinuities were found at 104 volts and 178 volts.

Copper.

The critical values obtained for this element were 112 volts and 193 volts, as indicated in the curves of fig. 6.

Fig. 6.



Zinc.

In the case of zinc the values obtained for the first critical voltage in different experiments varied over a wider range (some 8 volts in the extreme cases) than in the other elements investigated. The value most often obtained was 119 volts, at which point a discontinuity is indicated in the curve of fig. 7. The higher critical point obtained with this metal was at 200 volts.

In order to ascertain with which particular energy level the critical energy values which have been found in this investigation are to be associated, the Moseley curves for the various M absorption limits have been plotted and

Fig. 7.

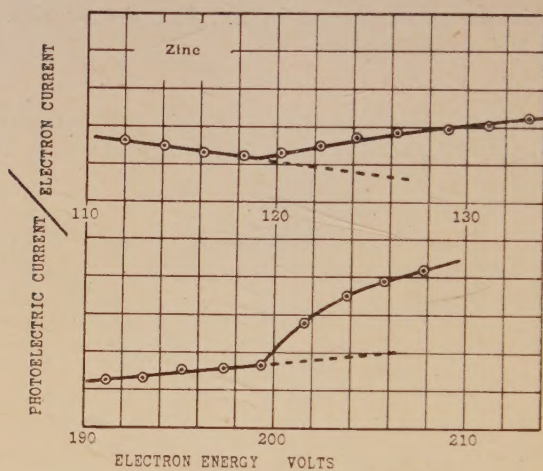
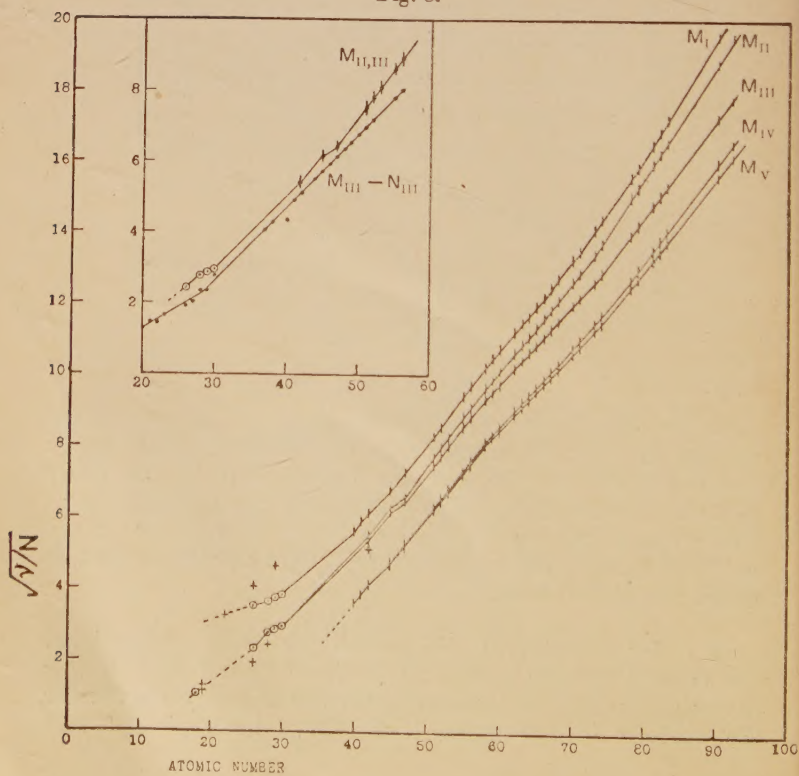


Fig. 8.



prolonged to low atomic numbers (see fig. 8). The square roots of the quantities ν/N , where N is the Rydberg constant and ν is the wave number, have been plotted as ordinates and the atomic numbers as abscissæ. Bohr's notation is employed throughout this paper for designating the various energy levels, and in referring to X-ray emission lines use is made of Siegbahn's notation as revised by Coster. The Moseley curves have been plotted for absorption limits rather than for emission lines because, in order to excite the lines associated with any particular level, it is presumably necessary to supply the energy required for the removal of an electron from the appropriate sub-group to the boundary of the atom, or at any rate to the first incomplete outer electronic group. Five M critical absorption wave-lengths have been measured spectroscopically for uranium ($z=92$) and for thorium ($z=90$) and three such wave-lengths for bismuth ($z=83$). Values of the various M critical absorption wave-lengths for elements of lower atomic number can be computed from the frequency relations given below for those cases in which the K and L absorption wave-lengths, and the K and L emission wave-lengths, have been measured directly:—

$$\begin{aligned} M_I &= L_{III} - L_I = L_{II} - L_{\eta}, \\ M_{II} &= K - K_{\beta_3} = L_I - L_{\beta_4}, \\ M_{III} &= K - K_{\beta_1} = L_I - L_{\beta_3}, \\ M_{IV} &= L_{III} - L_{\alpha_2} = L_{II} - L_{\beta_1}, \\ M_V &= L_{III} - L_{\alpha_1}. \end{aligned}$$

L critical absorption wave-lengths have been measured spectroscopically for ten elements between uranium ($z=92$) and tungsten ($z=74$) and for elements between neodymium ($z=60$) and antimony ($z=51$), and the necessary emission lines have been measured for most of these elements.

By using the frequency relations

$$\begin{aligned} L_{II} &= K - K_{\alpha_2}, \\ L_{III} &= K - K_{\alpha_1}, \end{aligned}$$

it is possible to compute the values of L critical absorption wave-lengths from observations of K absorption limits and K emission lines, and by using the values of the L absorption limits thus computed, to calculate the values of M_I , M_{IV} , and M_V from the relations already given, even in cases where L critical absorption wave-lengths have not been

measured directly. The quantities ν/N , and also the square roots of these, for the various M absorption limits have been worked out down to $z=40$ by Bohr and Coster*, much of their data being obtained from researches which have recently been carried out in Siegbahn's laboratory by Coster himself and others. These values have been used in plotting most of the curves shown in fig. 8, and points obtained from Bohr and Coster's tables of $\sqrt{\nu/N}$ are marked in this figure by short vertical lines across the curve. The lines for M_{II} and M_{III} , and those for M_{IV} and M_V , merge together for low values of the atomic number, as is readily seen. In the case of the $M_{II,III}$ level, Bohr and Coster give values of $\sqrt{\nu/N}$ for elements from $z=29$ to $z=13$, but these have not been marked in fig. 8 on account of their being very irregularly situated. Moreover, the accuracy of the computed values for the case of elements of low atomic number seems very doubtful, for if the values obtained for the K absorption limits by different observers are employed, very different values of the M absorption limit result from the computation. The percentage error in the computed value, resulting from a small error in the measurement of the K absorption limit or of $K\alpha_1$ or $K\alpha_2$, is very considerable because the two quantities whose difference has to be taken are so nearly equal for low atomic numbers.

The square roots of the quantities ν/N connected by the quantum relation with the critical voltages determined in this investigation for the elements iron ($z=26$), nickel ($z=28$), copper ($z=29$), and zinc ($z=30$) are marked in fig. 8 by circles, and the value of $\sqrt{\nu/N}$ corresponding to the ionization potential of argon ($z=18$) determined by Horton and Davies† is similarly marked. Values calculated from observations of other investigators, by the excitation potential method, are marked with a cross in fig. 8. The value for molybdenum ($z=42$) was calculated from data obtained by Richardson and Bazzoni‡, and the values for titanium ($z=22$), iron, and copper from experiments by Kurth§. A lower point obtained by Kurth for copper falls slightly below the smaller of the two values obtained by the authors for this element, but is not shown in fig. 8, since it would be indistinguishable from the point already marked. The

* N. Bohr and D. Coster, *Zeits. f. Phys.* xii. p. 6 (1923).

† E. Horton and A. C. Davies, *Proc. Roy. Soc. A*, xcvii. p. 1 (1920), and cii. p. 131 (1922).

‡ O. W. Richardson and C. B. Bazzoni, *Phil. Mag.* xlii. p. 1015 (1921).

§ *Loc. cit.*

values for potassium ($z=19$), and the value for nickel which is marked with a cross, were obtained by Mohler and Foote*.

The existence of the gap between the values calculated from spectroscopic data, and the values obtained from excitation potential methods, *i.e.* the gap between $z=40$ and $z=30$, makes it difficult to decide with certainty with which energy level the various values obtained in this research are to be associated. The general trend of the various lines suggests that the lower set of values are associated with the $M_{II,III}$ level, and that the upper set of values are associated with the M_I level. To obtain more definite evidence on this matter, however, another line was computed corresponding to $M_{III}-N_{III}$, and is shown in the lower of the two curves in the upper left-hand corner of fig. 8. The line was computed from the relations

$$(1) K_{\beta_2} - K_{\beta_1} = M_{III} - N_{III},$$

$$(2) L_{\gamma_3} - L_{\beta_3} = M_{III} - N_{III}.$$

For the elements between $z=56$ and $z=37$ the values were calculated from relation (2), using Hjalmar's determinations of the wave-lengths of some of the L emission lines by the precision method†, and Coster's determinations which were made with reference to Hjalmar's lines‡. For the elements $z=30$ to $z=20$ the values were calculated from relation (1), using recently obtained data collected by De Broglie§. It may be seen that, with the exception of the value for $z=40$, the points for atomic numbers between 56 and 37 lie very nearly on a straight line a little below the M_{III} line, part of which is plotted again in the same diagram for comparison with the $M_{III}-N_{III}$ line. The positions of the lower points on this latter line make it clear that the lower set of values obtained in this research for iron, nickel, copper, and zinc cannot be associated with the $M_{IV,V}$ line, for this line lies below the $M_{III}-N_{III}$ line while these four points (marked with circles) are above the $M_{III}-N_{III}$ line, as would be expected if they are to be associated with the $M_{II,III}$ level.

For comparison with the M_I curve a line was computed, from $z=56$ as far as $z=37$, corresponding to M_I-N_I from the relation $L_{\lambda_c} - L_{\gamma_c} = M_I - N_I$ and Coster's precision data. This line, which, to avoid confusion, is not shown in fig. 8, was just below the M_I line, and was considerably straighter

* F. L. Mohler and P. D. Foote, *Phys. Rev.* xviii. p. 94 (1921).

† E. Hjalmar, *Zeits. f. Phys.* iii. p. 262 (1920), and vii. p. 341 (1921).

‡ D. Coster, *Phil. Mag.* xliii. p. 1070 (1922).

§ *Les Rayons X*, p. 92.

than this, and when prolonged to atomic number 30 was above the lower set of points obtained in this research. Since the values for M_I cannot lie below the corresponding values on the $M_I - N_I$ curve, it seems reasonable to conclude that the lower set of points obtained in this research cannot be associated with the M_I level. The M_I line and the $M_{II, III}$ line have therefore been prolonged so as to connect with the upper set of ringed points, and with the lower set of ringed points, respectively. The two sets of values obtained in this investigation indicate that the curves do not proceed through the elements zinc, copper, nickel, and iron without suffering an inflexion. They therefore support the view that a change in the constitution of the M group, or in an inner electronic group, occurs in this region. In accordance with Bohr's theory, one would expect to find such an inflexion occurring at the element copper ($z=29$); but the observed points for zinc, copper, and nickel lie very nearly on two parallel straight lines, and the lines only show a clear deviation in passing from nickel to iron. Lack of information with regard to the region $z=40$ to $z=30$ makes it impossible to make definite statements with regard to inflexions in this part, but it seems possible that the inflexion occurs at zinc ($z=30$) instead of at copper*.

It will be seen from fig. 8 that the line for any one level is not straight, or even a continuous curve, but that it can be divided up into a series of approximately straight portions. To a close approximation the wave number of any absorption limit is given by the relation $\nu = N(z - c)^2 \frac{1}{m^2}$,

where c is a constant which differs for different levels and m has successive integral values—*e. g.*, 1 for the K level, 2 for the L levels, 3 for the M levels, and so on. In accordance with this relation, the graph of $\sqrt{\nu}/N$ against atomic number must be a straight line for any particular level so long as c remains constant. This quantity can, however, be looked upon as consisting of the sum of two quantities c_1 and c_2 , one of which, c_1 , depends upon the number of electrons in groups of smaller energy value than the one under consideration, and the other of which, c_2 , depends upon the number and arrangement of electrons in the group under

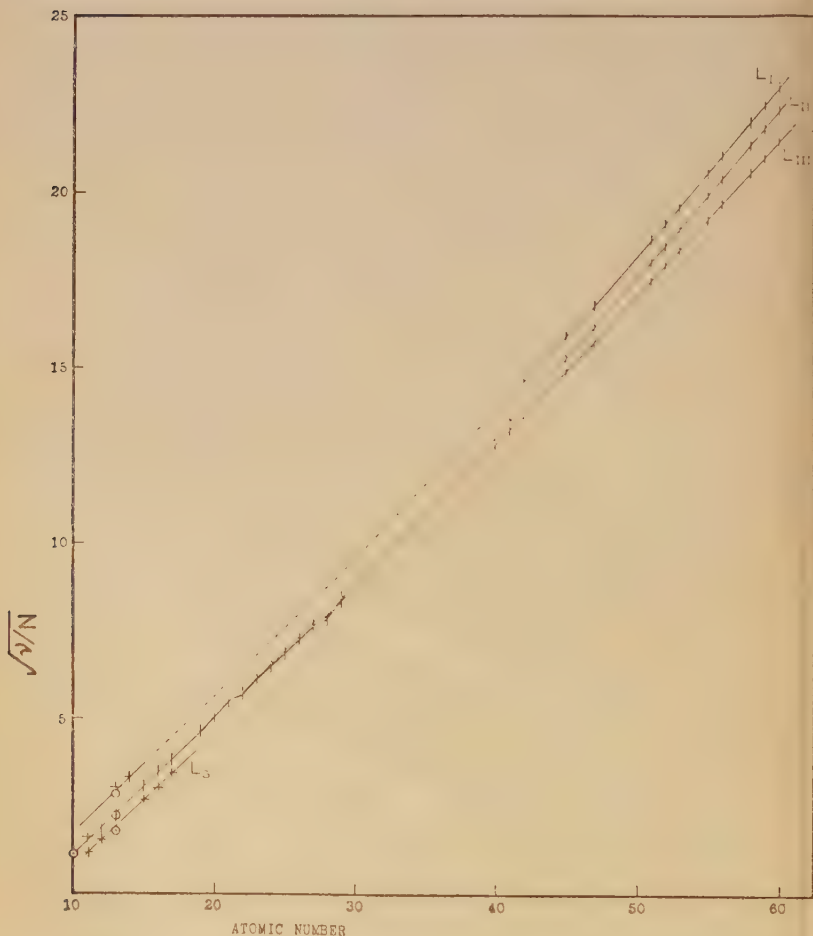
* Since the communication of this paper, it has been pointed out to the authors by Prof. Bohr and Dr. Coster that the fact that the valency of the elements in this region is not constant may prevent the change of slope in the curve occurring sharply at the element copper and may cause it to occur in a more gradual manner.

consideration, and in outer electronic groups. An increase in the number of electrons in such groups causes an increase in c_2 , this increase being greater if the change is in the number of electrons in the particular group itself than if it is merely in an outer group. Therefore, at any stage where an electronic group is in process of development, the quantity c_2 , and also the quantity c , corresponding to that group will increase more rapidly with increasing atomic number. The frequency ν of the corresponding absorption limit will therefore increase less rapidly with increasing atomic number, and the line should show a less steep portion extending from the element at which the change commences to the element at which the development of the group is complete. The upper parts of the lines given in fig. 8 for the various M levels show less steep portions at stages where, in accordance with Bohr's theory, changes in the constitution of the N group are in progress, this group being linked to a certain extent with the M group. Interpreted in this way, the fact that the lines for the M_I and $M_{II,III}$ levels are less steep over the regions titanium to zinc, and nickel to zinc, respectively, than elsewhere, supports the theory that the constitutions of the sub-groups with which these levels are connected are themselves changing in this region.

In accordance with the view that the M group at argon ($z=18$) consists of two sub-groups of four electrons each, while at copper it consists for the first time of three completed sub-groups each of which contains six electrons, the critical values found for argon and potassium must be associated with the $M_{II,III}$ level. The fact that between iron and nickel on the $M_{II,III}$ line the slope is considerably steeper than between nickel and zinc, and the fact that there is a steep slope for at any rate part of the way between argon and iron, suggests that the change in the second M sub-group occurs between nickel and zinc, or possibly between cobalt and zinc, but not before cobalt ($z=27$). That the slope of the M_I line appears to be less between titanium ($z=22$) and zinc ($z=30$) than elsewhere, may be taken to indicate that the change in the constitution of the first M sub-group commences at a lower atomic number than the change in the second M sub-group. It is probable that the irregularities in the slope of the lines between the various points is to be connected with the fact that a change in the constitution of one sub-group commences, and that then a change in the constitution of another sub-group begins before the first change is completed.

In order to ascertain with what absorption limits the values obtained for aluminium are to be associated, the Moseley curves for the various L absorption limits have been plotted downwards from $z=60$ (see fig. 9), using the values

Fig. 9.



of $\sqrt{\nu/N}$ worked out by Bohr and Coster. As in the case of the lines for the M absorption limits given in fig. 8, values obtained from the tables are marked by short vertical lines, values determined in this research by circles, while values obtained by other observers using the excitation potential

method have been indicated by crosses. Down to $z=51$ the critical absorption wave-lengths have been measured spectroscopically for many of the elements. Where the critical absorption wave-lengths have not been measured directly, it is possible to compute them, if the K absorption wave-lengths and the K and L emission wave-lengths have been measured, by using the two relations already given for L_{II} and L_{III} and the following for L_I :—

$$L_I = K - K_{\beta_3} + L_{\beta_1} = K - K_{\beta_1} + L_{\beta_3} = K - K_{\beta_2} + L_{\gamma_3}.$$

The spectroscopic data available enabled Bohr and Coster to determine the values of $\sqrt{\nu}/N$ as far as $z=12$ in the case of the $L_{II, III}$ absorption limit, but only as far as $z=42$ in the case of the L_I absorption limit. Apart from observations by the excitation potential method, the only direct information available with regard to the L absorption wave-lengths of elements of low atomic number is that provided by the work of Holweck*, who located the absorption limits of various elements by measurements of their absorption coefficients for the continuous radiation from a solid target under electronic bombardment. Holweck located an absorption limit for aluminium at a wave-length connected by the quantum relation with the voltage 64 ± 2 †, which agrees with the second critical value, 66 volts, found for aluminium in this investigation. The prolongation of the Moseley curves makes it clear that this critical voltage for aluminium ($z=13$) is to be associated with the $L_{II, III}$ level, and that the higher value (107 volts) is to be associated with the L_I level. The values for aluminium and silicon ($z=14$) marked with a cross were found by Kurth, and appear to be associated with the L_I level also.

The lowest discontinuity which we found in our curves for aluminium at 42 volts corresponds to a value of $\sqrt{\nu}/N$ which lies below the $L_{II, III}$ line, and which is therefore to be attributed either to some abnormal state of the L group or to the displacement of an electron from the second L sub-group to one of the M sub-groups instead of to the boundary of the atom. Mohler and Foote have found in the cases of sodium ($z=11$), magnesium ($z=12$), phosphorus ($z=15$), sulphur ($z=16$), and chlorine ($z=17$) similar discontinuities in their current-voltage curves at voltages below those which must be associated with the $L_{II, I}$ level. Hjalmar‡

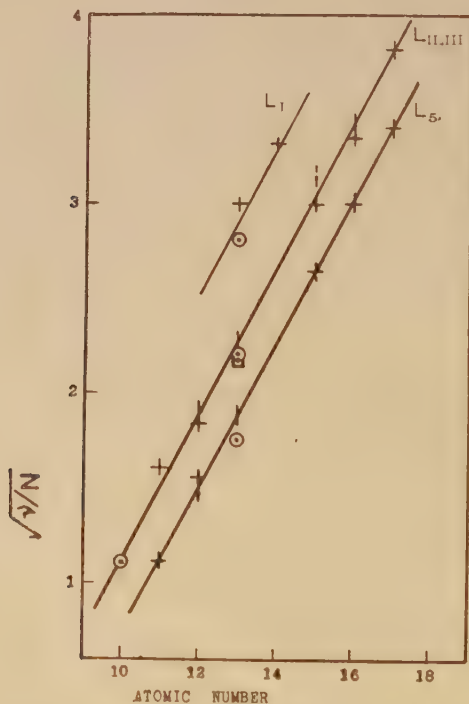
* M. Holweck, *Comptes Rendus*, clxxiii. p. 709 (1921).

† This point is shown in fig. 10, and is marked with a dot enclosed by a square.

‡ E. Hjalmar, *Phil. Mag.* xli. p. 675 (1921).

found for several elements in this region of atomic numbers, K emission lines which have no parallels in the X-ray spectra of the heavier elements. These lines he designates as α_1' , α_3 , α_4 , α_5 , α_6 , β_1' , and β' . Mohler and Foote associate the values of $\sqrt{\nu/N}$, which they obtained from their set of low discontinuities, with the occurrence of these additional lines. Using the relation $K - K\alpha_5 = L_5$, they compute values which when plotted according to the Moseley relation give a line parallel to the corresponding part of the $L_{II,III}$ line*. This line is shown in fig. 10, in

Fig. 10.



which diagram the lower parts of the $L_{II,III}$ line and the L_I line are drawn again on a larger scale than in fig. 9, the marking of the points being as already described. On the L_5 line the points computed from the differences $K - K\alpha_5$ are marked with vertical lines across the curve, the one for sulphur ($z=16$) being coincident with a point plotted from Mohler and Foote's observations. It may be seen that the

* 'The Origin of Spectra,' p. 208.

values of $\sqrt{\nu} N$ connected with Mohler and Foote's voltages lie either on, or very close to, this line. The line $K\alpha_5$ was observed by Hjalmar in the case of aluminium, and by computing L_5 from the relation given above and ascertaining the voltage connected by the quantum relation with the wave number so determined, the value 49.1 volts is obtained. This value is rather higher than the value (42 volts) which we determined experimentally for aluminium, so that it seems unlikely that our experimental value is to be associated with this hypothetical L_5 limit. Wentzel* has shown that the additional K emission lines observed by Hjalmar on the short wave-length side of $K\alpha_1$ are emitted by atoms which have lost more than one electron, and which have therefore absorbed more energy than that corresponding to the ordinary K absorption limit. If this is the case, then by taking the difference $K - K\alpha_5$ we do not obtain a quantity which has any true physical significance in the sense of an absorption limit. An L absorption limit on the *short* wave-length side of the usual limits might be expected if the simultaneous removal of two electrons from the L group took place, but it is difficult to see how an absorption limit on the *long* wave-length side of $L_{II, III}$ can be accounted for by such multiple ionization. The value (42 volts) obtained in our experiments must be connected with a genuine absorption limit, and not simply with a quantity which is calculated from the difference between a K absorption limit and a K emission line which corresponds to some exceptional state of the atom.

For the elements titanium ($z=22$), vanadium ($z=23$), and chromium ($z=24$) Fricke† found photographically an absorption discontinuity lying on the long wave-length side of the principal K discontinuity, and it has been suggested by Coster‡ that this anomalous discontinuity is to be connected with the removal of an electron from the K group to one of the incomplete M sub-groups. Such a suggestion receives support, as Coster has pointed out, from the discovery by Hjalmar of an emission line which he calls $K\beta'$, which has *exactly* the same wave-length as the anomalous discontinuity. The authors therefore think it probable that the critical stage which they obtained at 42 volts, in aluminium, and the low values found by Mohler and Foote for the elements sodium, magnesium, phosphorus, sulphur, and chlorine correspond to the displacement of an electron within the atom from the second L sub-group to one of the

* G. Wentzel, *Ann. der Phys.* lxi. p. 437 (1921).

† H. Fricke, *Phys. Rev.* xvi. p. 202 (1920).

‡ D. Coster, *Phil. Mag.* xliv. p. 546 (1922).

incomplete M sub-groups. According to Bohr's theory, the first M sub-group in aluminium contains two electrons and the second M sub-group contains one electron. The question arises as to which of these two incomplete M sub-groups receives the displaced electron at the 42-volt stage. If the electron enters the second M sub-group, we should expect $L_{II, III} - L_{(\text{anomalous})}$ to be comparable with the ionizing potential of the element of next higher atomic number. The difference between our values for $L_{II, III}$ and $L_{(\text{anomalous})}$ is 66 volts—42 volts=24 volts, however, a value which is considerably higher than the ionizing potential of most elements, so that it seems unlikely that the critical value at 42 volts for aluminium can be accounted for in this way. Moreover, a transition from the second L sub-group to the second M sub-group would not be in accordance with the selection principle, since the azimuthal quantum numbers of these two sub-groups are the same. It would appear then, that 42 volts corresponds to the energy necessary for the removal of an electron in the aluminium atom from the second L sub-group to the first M sub-group*.

Summary.

Investigations of the voltages connected with some of the longer wave-length absorption limits have been made for the elements aluminium, iron, nickel, copper, and zinc by the excitation potential method. The following critical values have been obtained :—

For aluminium...	42 volts, 66 volts, and 107 volts.
„ iron	73 volts and 166 volts.
„ nickel.....	104 „ „ 178 „
„ copper	112 „ „ 193 „
„ zinc	119 „ „ 200 „

By extrapolating the Moseley curves for the various absorption limits to low atomic numbers, the lower of the two

* It has been pointed out to the authors by Prof. Bohr and Dr. Coster that for elements of atomic number below about 24 the values of \sqrt{v}/N for $L_{II, III}$ given in their tables cannot be relied upon to the same extent as the values for higher atomic numbers, on account of the various electrical conditions of the atoms in the different compounds used in the experiments from which the data for the calculation were obtained. The possibility that the critical value of 42 volts for aluminium should be associated with the $L_{II, III}$ level, and the critical value 66 volts with the L_I level, while the highest value should be associated with some doubly ionized condition of the aluminium atom, cannot, therefore be entirely ruled out on the evidence at present in existence.

values obtained for each of the metals, iron ($z=26$), nickel ($z=28$), copper ($z=29$), and zinc ($z=30$), was found to be associated with the $M_{II,III}$ level, and the higher of the two values obtained for each of these elements was found to be associated with the M_I level. The changes in the slope of the M_I and $M_{II,III}$ curves in passing through the observed points support the view that a change in the constitution of the M electronic group is in progress as we pass from one of these elements to another. The results suggest that the development of the second M sub-group from four electrons to six electrons, as required by Bohr's theory, does not commence before the element cobalt ($z=27$), but that the similar development of the first M sub-group commences for a lower value of the atomic number.

By extrapolating the Moseley curves for the L absorption limits in a similar way, the two higher values found for aluminium have been connected with the L_I and $L_{II,III}$ levels respectively. From analogy with the anomalous K absorption limits found by Fricke for titanium, vanadium, and chromium, which Coster suggests are due to the displacement of an electron from the K group to an incomplete M sub-group, it seems probable that the lower value (42 volts) found for aluminium is to be associated with the displacement of an electron from the second L sub-group to the first M sub-group.

LXXXIV. *Vacuum Grating Spectrograph and the Zinc Spectrum.* By R. W. WOOD, *Professor of Experimental Physics, Johns Hopkins University* *.

[Plate XI.]

THE reproductions of spectrograms obtained with concave gratings mounted in vacuum spectrographs which have been published during the past five years appear to indicate that higher resolving power in the short wave-length region is very much to be desired, if accurate determinations of wave-length are to be made.

During the past winter I have made some preliminary investigations with two instruments of this type which have been constructed in the shop of the University.

In view of the present grating situation it appears to be worth while to publish a brief statement of what may be

* Communicated by the Author.

expected of short-focus concave gratings, which can now be produced on the Rowland engines as desired.

A good deal of time was spent in getting the spectrograph into proper condition, as much trouble was found owing to the presence of absorbing vapours, and at the close of the University year but two satisfactory spectrograms had been obtained, one of carbon and one of zinc, with carbon as an impurity. The lines on these two plates, however, were sharper than any that I have ever seen, and the focus appeared to be perfect over the entire range of the plate.

A three-fold enlargement of the zinc spectrogram is reproduced in Plate XI. *a* in coincidence with a corresponding portion *b*, of the spectrum enlarged to the same scale from the reproduction accompanying Sawyer's paper on the Zinc spectrum, published in the 'Astrophysical Journal' for December 1920.

Certain groups of lines, enlarged 7.5 times, are reproduced at *c*, and immediately above these, small regions of these groups, enlarged 34 times, are given. It is only in these last that the lines show a width comparable with the width of the lines in Sawyer's spectrum. The corresponding portions of spectrum, in the series of enlargements, are indicated by brackets. This spectrum will be discussed more fully presently.

The Spectrograph.

The spectrograph was constructed along lines similar to those indicated in Prof. McLennan's paper, published recently in the Proceedings of the Royal Society. Certain modifications, intended to facilitate the operation and adjustments of the instrument, were introduced, but will be passed over without comment, as, in the opinion of the writer, the best type of vacuum spectrograph is yet to be designed. Through a misunderstanding on the part of the mechanic, the large conical ground joints were put together with alcoholic shellac, the vapour from which was doubtless responsible for the failure of the instrument to record anything below wave-length 1600 for several weeks. With continued operation, however, the range gradually increased until a group of lines at 834 appeared, the limit obtained up to the present time. With more rapid methods of exhaustion, however, and continued operation, matters will undoubtedly improve. Up to the present time I have given but little attention to the design of the instrument, being occupied

chiefly with the question of the best type of grating to employ. Thus far but one grating has been ruled, but as it appears to yield spectra of high quality with comparatively short exposures, a brief description of it may not be out of place.

The Concave Grating.

Owing to the difficulties found in securing a sufficiently constant temperature in the dividing-engine room, practically no gratings have been ruled on the Rowland machines since the removal of the Physical Laboratory to its temporary quarters in the Electrical Engineering Building six years ago. The walls of the small room are exposed to the outer air on two sides, and the gas-heated radiator controlled by a thermostat was found to be useless, as the flame was frequently blown out by air blasts from outside.

Having need of a short-focus grating for a recently constructed vacuum spectrograph, I took up the problem of securing proper conditions for ruling last autumn. The gas radiator was removed, and the inlet and exhaust pipes through the wall closed. In its place was installed a small gas stove of sheet iron, heated by a ring of small bat-wing burners. This type of flame was chosen in preference to the bunsen flame, as it can be turned down indefinitely without snapping back. The stove was provided with a chimney of sheet iron about 12 feet long, which passed out through the wall into the corridor. The gas supply was regulated by a toluene thermostat, the rising mercury column closing a glass tube perforated with a very minute hole a little above its open end. This hole served as a by-pass for gas in sufficient quantity to maintain flames about 2 cms. in height, furnishing enough heat to keep the room several degrees above that of the outside air in the warmest weather.

This arrangement has given perfect satisfaction, the temperature in the room having held constant to within $0^{\circ}.2$ throughout the winter and spring. Except when sudden and extreme temperature changes occurred outside, the changes in the room were not over $0^{\circ}.1$.

While this is satisfactory for short-focus gratings of moderate resolving power, a better control was desirable for ruling very large gratings of high resolving power. To meet this requirement a large grid of very fine insulated resistance wire was set up in the glass cage in which the

engine operates. The heating of this grid by a 110-volt current is so slight that it cannot be felt by the fingers. A toluene thermostat will control the current, and judging from results found in controlling the temperatures of gratings during long exposures, I feel sure that the engine can be operated continuously at a temperature which is constant to within $0^{\circ}01$.

From a number of trial rulings a setting of the diamond was selected which gave a light brown colour in the central image, and a symmetrical distribution of the light in the spectra to the right and left. Professor Millikan has stated that he believes that the rulings best suited for work in the Lyman region are made with so light a touch that some of the original polished surface is left undisturbed. I was unable, however, to convince myself by examination with a $\frac{1}{12}$ inch immersion objective and vertical illumination that such was the case, except in one instance where the ruling was so light that markings were left by the diamond only on the softer crystals of the mosaic of which the speculum alloy is made. Such rulings were obviously unfit for use, and I accordingly chose one not much lighter than those usually employed. The microscope gave no indication that any of the original surface of the concave plate remained, and there was no marked concentration of light in any one spectrum.

The radius of curvature of the plate was one metre, and it was ruled with 15,000 lines to the inch, the ruled surface measuring about 1×4 inches.

The exposure times required with this grating were not longer than those recorded by other investigators working under similar conditions.

The Electron-Arc.

The source of light employed was the peculiar type of discharge which I described somewhat fully in 1897*.

In this paper it was shown that an intermittent arc-like discharge could be made to pass between two beads of platinum or other metal, separated by a distance of about 1 mm., if a source of high potential with a spark-gap in circuit was employed. It was found that the anode was rapidly eaten away, the spherical bead eventually becoming

* R. W. Wood, "A new type of Cathode discharge and the production of X-rays, together with some notes on diffraction," *Physical Review*, July 1897.

hemispherical in form, while a deposit of the metal was built up on the cathode. The surface of the anode upon which the arc played was found to be a very powerful source of X-rays, the intrinsic intensity being from 10 to 20 times as great as that from the focus tubes available at the time, the bones of the arm showing distinctly in a fluoroscope with a radiating source of about one square millimetre.

From a study of the source of the X-radiation by pinhole photography, I came to the conclusion that the cathode rays, which went off in all directions from the negative ball and wire when no spark-gap was included, were, by the introduction of the gap, gathered into a dense bundle between the ball electrodes, but that a few escaped and played around the ball, impinging upon the supporting wire almost, if not quite, down to the point at which the wire joins the ball. This type of discharge has been subsequently observed and studied by other investigators, and is usually referred to as the "hot-spark." I suggested its use on several occasions many years ago as a promising method of obtaining metallic spectra in the region of very short wave-lengths, but having no vacuum spectrograph, I never put it to this use. Professor Millikan has, however, employed it in this way, with most brilliant results, as is well known. The new Lilienfeld X-ray tube appears to operate on a somewhat similar principle. In this tube a pointed cathode is mounted at a distance of a millimetre or two from a concave anode in a very high vacuum. The electrons are drawn out of the pointed cathode in a dense stream by the very strong electric field, and raise the anode cup to a white heat. The discharge itself, however, is non-luminous in this case, I am told.

In the present instance the discharge was operated by a 30,000-volt transformer, with two large leyden-jars and a spark-gap of about a centimetre. Discharges of very brief duration only were employed, as continued operation caused too great an evolution of gas for the slow exhaustion through the slit to take care of, and resulted in a diffuse glow discharge which filled the small bulb in which the electrodes were mounted. The short flashes were obtained by striking the primary wires of the transformer together at intervals of about one second, the time of contact being so brief that only a single flash occurred. About 1000 flashes gave a fully exposed plate, and required only about twenty minutes. Schumann plates made by the Hilger Co. were employed.

Discussion of the Spectra.

With a grating of only one metre radius a very fine slit must be employed, and the focus determined to within 0.5 mm. to secure the best results. It does not appear as if anything could be gained by the use of a bent plate.

If we compare the spectrum reproduced in Plate XI. *a*, with the zinc spectrum published by Sawyer (*b*), the first thing that strikes our attention is the relative weakness of the latter in the region around 1500. My plate shows a very strong triplet at 1500, no trace of which is given by Sawyer's plate. This line is not a true triplet in all probability, and its origin is unknown, though the two stronger members agree closely in position with two Silicon lines on one of Prof. Fowler's photographs. The zinc rods which I used were not chemically pure, though of better quality than ordinary battery rods.

My plate shows a far greater number of lines than Sawyer's, and I believe that most of them are due to zinc.

In the region between $\lambda = 1283$ and $\lambda = 1500$ are recorded 96 lines against 14 in Sawyer's table.

The carbon line 1036.1 given by Sawyer is, on my plate, a clearly separated doublet, 1037.14 and 1037.50 (Simeon's determination of wave-length).

It seems probable that the weak region on Sawyer's plate around 1500 was due to the presence of some absorbing vapour in his spectrograph. My plate is very weak between 980 and 1240, while Sawyer's shows a very strong group of lines in this region. I find faint records of all of Sawyer's lines between 976 and 1066, but no trace of the 10 lines which he gives between 1066 and 1165. All of the lines of longer wave-length given by Sawyer appear on my plate. It seems evident that absorbing vapour must have been present in both instances, alcohol probably in my case.

The 7.5-fold enlargement of portions of the original spectrogram were made with a microscope fitted with a 16 mm. objective: the 34-fold enlargements were made with a 4 mm. objective. Comparison of these last with Sawyer's spectrogram indicates that the lines on his plate were about 12 times as wide as mine.

He gives, in his table of wave-lengths, the carbon triplet, resolved by Simeon in the second order spectrum (1561.32, 1560.67, 1560.16) as a single line of wave-length 1561.1. My plate shows it as a doublet, with components of equal

intensity and a separation of one Ångström unit. This I cannot reconcile with Simeon's observation, as he gives his lines intensity values of 8, 9, 9, and separations of 0.65 and 0.51.

Simeon's paper on the carbon spectrum in the extreme ultra-violet was published in the *Proc. Roy. Soc.* vol. 102, p. 717. He photographed the zinc lines of the second order spectrum in coincidence with the iron comparison spectrum of the first order, obtaining in this way a far higher degree of precision in his wave-length determinations than in the cases in which the position of lines with reference to the central image is measured.

I was in hopes that, by using Simeon's carbon lines as standards, a fairly accurate table of wave-lengths could be prepared of the zinc lines shown on my plate, on which carbon appears as an impurity. After measuring both my carbon and zinc plates twice, and spending several days on the computations, I have decided, however, to wait until other spectrograms, using pure substances, have been obtained. The spectrum is not quite normal and there are too few carbon lines on my zinc plate, except in the region between 1000 and 1300, for the proper determination of the corrections to be applied.

My carbon and zinc spectra are also not quite on the same scale, due probably to the fact that the temperature of the instrument was not the same in both cases. This makes it impossible to calibrate my zinc plate, with its few carbon lines, from the carbon plate with many lines. Sawyer's table does not include the very strong carbon double line 1335.66, 1323.79 (one of the strongest on my plate), though he finds numerous lines of less intensity. This line, however, lies in the region in which his spectrum is very weak, while mine is very strong at this point. If the absorption spectrum of the vapour in his spectrograph was discontinuous, *i. e.*, channelled like the spectrum of benzine, it might suppress some very strong lines and pass others of less intensity.

I feel quite sure that an accuracy of .05 Ångström will be possible with plates made with proper precautions, that is, assuming Simeon's values of the carbon lines to be correct to this order of accuracy, which I believe to be the case. The error involved in the settling of the cross-hair on the lines of my plate, when translated into wave-lengths, amounted to only 0.03 Ångström, and lines separated by 0.3 Ångström were resolved without difficulty.

While determinations of wave-lengths for the entire spectrum must be deferred until more satisfactory comparison spectra have been secured, I will give a short table of the values found in the region between 1600 and 1930, where practically all of the lines agree in position with lines found by Sawyer with pure zinc, and in addition the lines in the region between 1000 and 1300, where the accuracy is somewhat greater. I believe that all of the values are correct to 0.1 Ång. Sawyer's values are given in a parallel column, together with a column of differences.

TABLE I.

Int.	Zinc λs.		Dif.
	(Wood).	(Sawyer).	
0	1918.67	1919.6	+ .93
0	1863.96	1864.4	+ .44
4	1839.21	1838.8	- .41
1	1833.54	1833.3	- .24
1	1822.05		
0	1811.18	1811.10	- .18
0	1808.23		
6	1767.79	1767.5	- .29
1	1754.04	1753.4	- .64
8	1749.87	1749.4	- .47
6	1707.18	1706.3	- .88
2	1695.49	1695.4	- .09
7	1688.72	1688.5	- .22
10	1673.21	1672.7	- .51
0	1657.86	Carbon.	
1	1657.26		
00	1656.61		
7	1651.94	1651.5	- .44
8	1645.05	1644.7	- .35
9	1639.54	1639.1	- .44
9	1629.43	1629.3	- .13
7	1622.87	1622.8	- .07
6	1620.01	1619.6	- .41
6	1601.15	1601.4	+ .25

Assuming my values to be correct to the order of 0.1 Ångström, the errors in Sawyer's table show a maximum value of ± 0.1 Ång., which seems to be about what is to be expected, in view of the fact that his lines were about ten times wider than mine : this, of course, is on the assumption that his measurements were made from the plate which was reproduced with his paper, which may not have been the case.

The following values were obtained further down the spectrum :—

TABLE II.

Int.	Wood.	Sawyer.	Dif.
2	1307.32		
5	1306.50	1306.1	+ .40
0	1304.71		
2	1303.55		
1	1301.20		
0	1298.47		
1	1296.59		
2	1295.28		
3	1292.21	1293.3	-1.09
0	1291.84		
0	1289.98		
00	1284.58		
00	1283.54	1282.9	+ .64
00	1281.35		
0	1280.34		
00	1278.91		
0	1277.03		
0	1276.24		
1	1274.41		
2	1272.88	1273.1	
2	1272.06		
00	1270.76		
0	1268.15		
3	1265.63	1264	+1.63
3	1262.68		
3	1253.29	1252.5	+ .79
00	1250.24		
00	1249.89		
2	1247.2 Carb.		
3	1228.34	1228.6	- .26
0	1223.41	1223.1	+ .31
0	1215.51 Hydrogen.	1215.9	- .39
0	1204.26		
0	1203.65	1201.5	
0	1200.63		
0	1195.21	1194.6	+ .61
0	1066.3 Carb.		
5	1048.86	1048.8	+ .06
8	1036.84 Carb.	1036.1	+ .74
0	1028.57	1029.8	-1.23
6	1010.11 Carb.	1009.3	+ .81
0	1001.58	1001.2	+ .38
0	834.21		
0	833.08		
0	832.73		

The degree of accuracy of the wave-lengths given in this table may be inferred from the value found for the hydrogen line 1215.51. Simeon gives it as 1215.53.

The carbon line 1010.11 was also a calculated value : Simeon's value is 1010.09.

The region given in this table is the one which is extremely weak on Sawyer's spectrogram, and the fact that he finds

but two of the three strong lines 1265, 1262, and 1253 may be perhaps taken as evidence that the absorption band of the vapour in his spectrograph was discontinuous. Additional evidence of discontinuous vapour absorption is given by my plates.

The carbon quadruple line at 1657, which Simeon finds of the same intensity as the triple line at 1560, appears on my plate of the carbon spectrum as a triple line of intensity greatly inferior to that of a double line at 1560. On the zinc plate, however, the triplet is recorded, but there is no trace of the doublet. It seems quite probable that the vapours given off by the electron-arc in the two cases may have shown a different selective absorption. With the arrangements for pumping employed, these vapours entered the spectrograph through the slit. This will be avoided in future work.

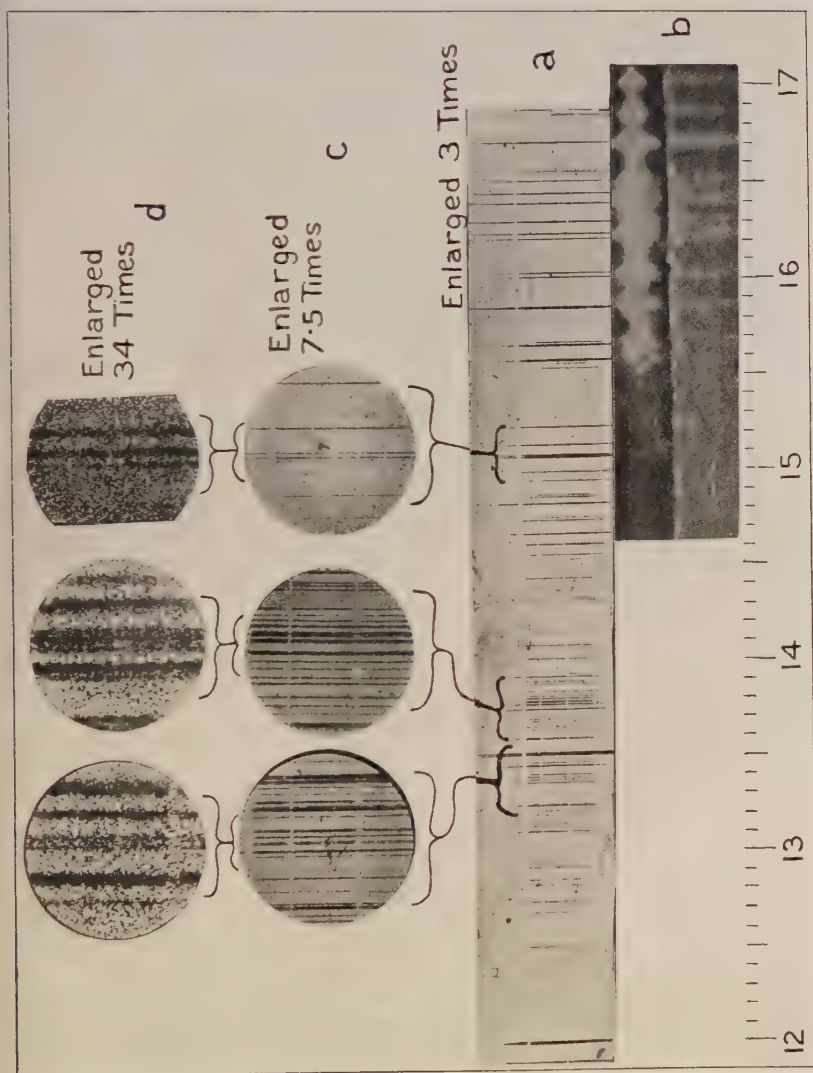
Lyman Ghosts.

Some results obtained in the early part of the work, while adjusting and focussing the grating with the aluminium spark as a source of light, led me to take up a study of the Lyman Ghosts shown by the grating. These appear in the region between 1200 and 2000 of the first order spectrum when the spectroscope is filled with air. They are attributed to a periodic error of the order of magnitude of the distance between five or six lines of the grating. Apparently only spectra of higher order than the fifth or sixth were produced by this periodicity, for no trace of the ghosts appeared in the vicinity of the central image.

No trace of them can be seen with visible light, when the quartz mercury arc in combination with a green screen is viewed in the grating, and no trace appears on photographs made with a one-hour exposure with the quartz arc screened with nickel oxide glass, which transmits Hg 3660 at nearly its full intensity.

With an exposure of 1 hour with a naked quartz Hg arc, cooled by water, which emits the 2536 radiation with a terrific intensity, faint traces were secured, while a one-minute exposure to the light of the aluminum spark brought them out strongly.

All of these circumstances, taken together, make me feel that there is still something to be found out in regard to the causes operating in the production of the Lyman Ghosts, the study of which will be continued in the autumn, with different types of monochromatic sources, and with gratings in the ruling of which the driving power of the motor is transmitted to the ruling engine in different ways.



LXXXV. *The Stark Effect for Strong Fields.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

THE appearance in your May issue of a letter by Mr. H. O. Newbould dealing with two recently-published papers of mine* on the Stark Effect for Strong Fields, makes it necessary that the details of the correct solution, roughly indicated in my second paper, should be published. The following are the main steps of the analysis with the same notation as before, except where it is specified to the contrary, corresponding equations being denoted by the same numbers:—

As pointed out in the second paper, equation (7) should assume the form

$$B = -\sqrt{A} \left(\sqrt{C} + \frac{n\hbar i}{\pi} \right) + \frac{D}{4A} \left(C - \frac{3B^2}{A} \right) + \frac{5BD^2}{16A^3} \left(3C - \frac{7B^2}{A} \right), \quad (7)$$

where one of the suffixes 1 or 2 may be attached to the set of letters (A, B, C, D, n), the eight quantities $A_1, A_2, \dots, D_1, D_2$ being given by equations (5a) and (5b) of the first paper, and n_1, n_2 being quantum numbers.

Equations (12) and (13) should also read

$${}^0B^2 = A_0 \left(\sqrt{C} + n\hbar i/\pi \right)^2, \quad (12)$$

$${}^1B^2 = A_0 \left(\sqrt{C} + n\hbar i/\pi \right)^2 \mp \frac{\hbar^4(n_1+n_2+n_3)}{32m_0eE^2\pi^4} \sqrt{A_0N} \left(\sqrt{C} + \frac{n\hbar i}{\pi} \right) F, \quad (13)$$

where the notation 0, 1, ... etc. placed above the quantity refers to 0, 1st, ... etc. orders of approximation in the field F respectively. And on substituting for B in the last two terms of (7) from (13) and (12) respectively, we have

$$B = -\sqrt{A} \left(\sqrt{C} + \frac{n\hbar i}{\pi} \right) \mp \frac{m_0eF}{4A} \left\{ C - \frac{3A_0}{A} \left(\sqrt{C} + \frac{n\hbar i}{\pi} \right)^2 \right. \\ \left. \pm \frac{3\hbar^4(n_1+n_2+n_3)\sqrt{A_0NF} \left(\sqrt{C} + \frac{n\hbar i}{\pi} \right)}{32m_0eE^2\pi^4 A} \right\} \\ - \frac{5m_0^2e^2F^2}{16A_0^5} \left(\sqrt{C} + \frac{n\hbar i}{\pi} \right) \left\{ 3C - 7 \left(\sqrt{C} + \frac{n\hbar i}{\pi} \right)^2 \right\}, \quad (14)$$

* Phil. Mag. xliii. p. 943 (1922), and xliv. p. 371 (1922). These will be referred to as the "first paper" and "second paper" respectively.

or on adding corresponding sides of the two equations embodied in this :

$$\begin{aligned}
 m_0 e E = - \sqrt{A} \frac{(n_1 + n_2 + n_3) \hbar i}{2\pi} \\
 + \frac{3m_0 e A_0}{2A^2} \frac{\hbar^2 (n_2 - n_1) (n_1 + n_2 + n_3)}{(2\pi)^2} F \\
 - \frac{3i \sqrt{A_0} \hbar^5 N (n_1 + n_2 + n_3)^2}{8 \times (2\pi)^5 E^2 A^2} F^2 \\
 - \frac{5m_0^2 e^2 F^2 i \hbar^3}{8 \times (2\pi)^3 A_0^{5/2}} (n_1 + n_2 + n_3) R, \quad (15)
 \end{aligned}$$

where *

$$R = \frac{7}{2} (n_1 + n_2 + n_3)^2 + \frac{21}{2} (n_2 - n_1)^2 - \frac{3}{2} n_3^2. \quad (15a)$$

We proceed to solve for A by putting

$$A = -(K + LF + MF^2), \quad (16)$$

so that

$$\left. \begin{aligned}
 \sqrt{A} &= i \sqrt{K} \left(1 + \frac{1}{2} \frac{L}{K} F + \frac{1}{8} \frac{4MK - L^2}{K^2} F^2 \right) \\
 &\quad \text{approximately,} \\
 \frac{1}{A^2} &= \frac{1}{K^2} \left(1 - \frac{2L}{K} F \right) \\
 &\quad \text{,,}
 \end{aligned} \right\} \quad (17)$$

And on equating the coefficients of powers of F on the two sides of (15) respectively,

$$\left. \begin{aligned}
 m_0 e E &= \frac{\hbar \sqrt{K}}{2\pi} (n_1 + n_2 + n_3), \\
 0 &= \frac{\hbar L (n_1 + n_2 + n_3)}{2(2\pi) \sqrt{K}} - \frac{3m_0 e \hbar^2 (n_1 + n_2 + n_3) (n_2 - n_1)}{2(2\pi)^2 K}, \\
 0 &= \frac{(n_1 + n_2 + n_3) \hbar}{8 \times (2\pi) K^{3/2}} (4MK - L^2) \\
 &\quad + \frac{3m_0 e L (n_2 - n_1) (n_1 + n_2 + n_3) \hbar^2}{(2\pi)^2 K^2} \\
 &\quad + \frac{3(n_1 + n_2 + n_3)^2 \hbar^5 N}{8 E^2 (2\pi)^5 K^{3/2}} - \frac{5m_0^2 e^2 \hbar^3 (n_1 + n_2 + n_3) R}{8 \cdot (2\pi)^3 K^{5/2}},
 \end{aligned} \right\} \quad (17a)$$

* This function R is here introduced in order to facilitate comparison with Mr. Newbould's analysis.

giving

$$K = \frac{(2\pi)^2 m_0^2 e^2 E^2}{(n_1 + n_2 + n_3)^2 h^2}, \quad \dots \quad (18)$$

$$L = \frac{3h^2}{(2\pi)^2 E} (n_2 - n_1)(n_1 + n_2 + n_3), \quad \dots \quad (19)$$

$$M = \frac{L^2}{4K} - \frac{6m_0 e h L}{(2\pi) K^3} (n_2 - n_1) - \frac{3h^4 N (n_1 + n_2 + n_3)}{4 \times (2\pi)^4 E^2 K} \\ + \frac{5m_0^2 e^2 h^2}{4(2\pi)^2 K^2} R, \quad \dots \quad (20)$$

and after some reduction

$$M = \frac{h^6 (n_1 + n_2 + n_3)^4}{4 \times (2\pi)^6 (m_0 e E^2)^2} \left[5R - 63(n_2 - n_1)^2 - \frac{3N}{n_1 + n_2 + n_3} \right]. \quad (21)$$

And, further, on using (15 a) and the identity (quoted in the second paper) for N , viz.

$$N = (2n_1 + n_3)(6n_2^2 + 6n_2 n_3 + n_3^2) \\ + (2n_2 + n_3)(6n_1^2 + 6n_1 n_3 + n_3^2) \\ \equiv 3(n_1 + n_2 + n_3)^3 - 3(n_1 + n_2 + n_3)(n_2 - n_1)^2 \\ - n_3^2(n_1 + n_2 + n_3).$$

We have for the energy W the expression

$$W = - \frac{(2\pi)^2 m_0 e^2 E^2}{2(n_1 + n_2 + n_3)^2 h^2} - \frac{3h^2 F}{2(2\pi)^2 m_0 E} (n_2 - n_1)(n_1 + n_2 + n_3) \\ - \frac{h^6 F^2}{16(2\pi)^6 m_0^3 e^2 E^4} N', \quad \dots \quad (23)$$

where N' is given by

$$N' = 10R - 126(n_2 - n_1)^2 - \frac{6N}{n_1 + n_2 + n_3} \\ = (n_1 + n_2 + n_3)^4 \{ 17(n_1 + n_2 + n_3)^2 - 3(n_2 - n_1)^2 - 9n_3^2 \}. \quad (22)$$

This is the result quoted in the second paper.

The Manor House,
Alphington, nr. Exeter,
July 9th, 1923.

Yours faithfully,
A. M. MOSHARRAFA.

LXXXVI. *On Eddies in Air.* By HIRATA NISI and
ALFRED W. PORTER, *D.Sc., F.R.S., F.Inst.P.**

[Plate XII.]

THE following investigations were begun by one of us before the war, but preliminary observations only had been taken when the work had to be suspended.

The turbulent motion of a viscous fluid through a pipe has been studied by many investigators, including Osborne Reynolds, the late Lord Rayleigh, Rücker, Stanton; but there is no complete mathematical solution for the motion of a viscous fluid past a solid obstacle, especially when the motion is so fast that eddies are produced. Such solutions as have been given neglect the effect of inertia terms; for example, those of Stokes †, Oseen ‡, Williams §. They can hold therefore only when the velocity is small and the viscosity is great.

There are many papers || dealing with eddies behind an obstacle, and no doubt there are others which have not yet been published; most of them refer to liquids only.

Although the law of dynamic similarity holds independently of the particular fluid concerned (water, air, etc.), we should bear in mind that when there are very great differences in the properties (density, viscosity, etc.) of the fluids compared, the *approximate* law that may have been found to be sufficiently good for one case may be inapplicable to another.

The present paper is concerned with the eddies which form in air which flows past obstacles of various forms; it is divided into three parts.

The first deals with the relations between the dimensions of the obstacles and the critical velocities at which eddies begin to form when the air flows through an air-channel containing the obstacle. Smoke drawn through with the air was used as an indicator. The second deals with the velocity distributions in the eddies and surrounding fluid. Thirdly,

* Communicated by the Authors.

† Lamb, 'Hydrodynamics,' pp. 591, 596 (1916).

‡ Williams, *Phil. Mag.* xxix. p. 525 (1915).

§ Lorentz, *Ab. ii. Theoretische Physik*, xxxix. (1907).

|| Ladenburg, *Ann. d. Phys.* xxiii. p. 447 (1907); Bénard, *C. R.* cxlvii. p. 839 (1908); Mallock, *Proc. Roy. Soc. A.* lxxxiv. p. 482 (1910-11); Kármán & Rubach, *Phys. Zeitsch.* xiii. p. 49 (1912); Föppl, *Münch. Sitzungsb.* p. 1 (1913); Naylor & Frazer, Reports and Memoranda of Advisory Committee for Aeronautics, No. 332 (1917).

the relation between the mean velocities of flow and of the positions of the eddy-centres was obtained.

The general arrangement of the apparatus is as follows:—

Water from the mains flows into an eleven-litre vessel displacing the contained air which flows successively through a vessel where it picks up smoke and a U-tube (immersed in water) where its temperature becomes equalized. It then enters the air-channel in which the obstacle is mounted. Two sizes of square-sectioned channel were employed, both of brass. The larger one measured $2.6 \times 2.6 \times 30$ cm., the smaller was $2.0 \times 2.0 \times 25$ cm.

The method of examination was the same as in ultramicroscopy. In the middle of the brass channel small windows were cut and covered with thin glass plates. Light from a lantern could thus be passed horizontally across the obstacle, and the scattered light examined from above on a camera screen; or alternatively, photographs of the scattered light were obtained. Extensions were put on at each end of the chamber, and at the end of the inlet a piece of gauze inserted to make the stream as uniform as possible. The obstacle was mounted on a wooden plug, which was inserted through a hole in the bottom of the chamber: this plug was rotated in each case until the most symmetrical eddies were formed.

Suitable lenses were used to focus the light, one of them being a cylindrical lens to spread it out into a horizontal sheet in the axial plane of the channel in the neighbourhood of the obstacle. Heat filters were employed to minimize the heating effect.

The camera was furnished with a microscope objective of 2.5 cm. focal length. The image obtained was examined on the focussing screen by means of a simple magnifier; and when suitably steady figures formed by the smoke particles were obtained, the screen could be replaced by a photographic plate and a photograph was taken. But in many cases eye observations only were necessary.

PART I.

The relations between the dimensions of the obstacles and the critical velocities.

The obstacles employed were:—

A. *Spheres*: steel ball-bearings of nine different sizes, ranging from 1.59 to 7.94 mm. diameter. These were attached to fine embroidery-needles (diameter = 0.34 mm.) which served

as supports; only the smallest necessary amount of solder being used. The spheres as mounted were adjusted to the axial plane of the chamber; care was taken to adjust it as symmetrically as possible, the success in the adjustments being judged from the symmetry of the motion of the particles. The velocity of the stream was adjusted until eddying began. As the velocity is increased further the eddies become larger, their centres become more widely separated and their distances from the obstacle increase. The velocity at which the eddies begin was determined from the time taken to fill a definite portion of the eleven-litre vessel. The temperature of the air stream was observed. Tobacco smoke was used. From five to ten observations of the critical velocity were obtained for each sphere. A very small light-stop had to be used to make the heating effect negligible.

If the dimensions of the channel could be taken as infinite, the physical data determining the critical velocity would be the viscosity, μ , and density, ρ , of the air, and the diameter, d , of the obstacle. The method of dimensions then leads to Osborne Reynolds' equation

$$v_c = A \frac{\mu}{\rho d},$$

where A is a constant. In reality, however, the dimensions and form of the channel have some influence. The factor A is then a numerical function involving the diameter D of the channel. We shall assume as an approximation that

$$v_c = \frac{\mu}{\rho d} \left\{ A_1 + A_2 \left(\frac{d}{D} \right)^n \right\},$$

where A_1 and A_2 are constants.

All the experimental results at different temperatures were reduced to 20°C ., assuming Sutherland's formula as modified by Fischer* for the temperature coefficient of viscosity.

The above formula was found to fit nearly for different spheres and channels if n is taken as $3/2$. This was tested by plotting $\frac{v_c d \rho}{\mu}$ against $\left(\frac{d}{D} \right)^n$, as shown in fig. 1.

The values of A_1 and A_2 are 8.15 and 68.2 respectively.

Some doubt may be felt in regard to the influence of the supporting needle. This was tested by replacing it in the case of the smallest sphere by a fine hair-spring of a watch

* Phys. Rev. xxiv. p. 385 (1907).

(0.27 mm. \times 0.07 mm.). No difference was detected that would affect the general slope of the curve.

Fig. 1.—Sphere.



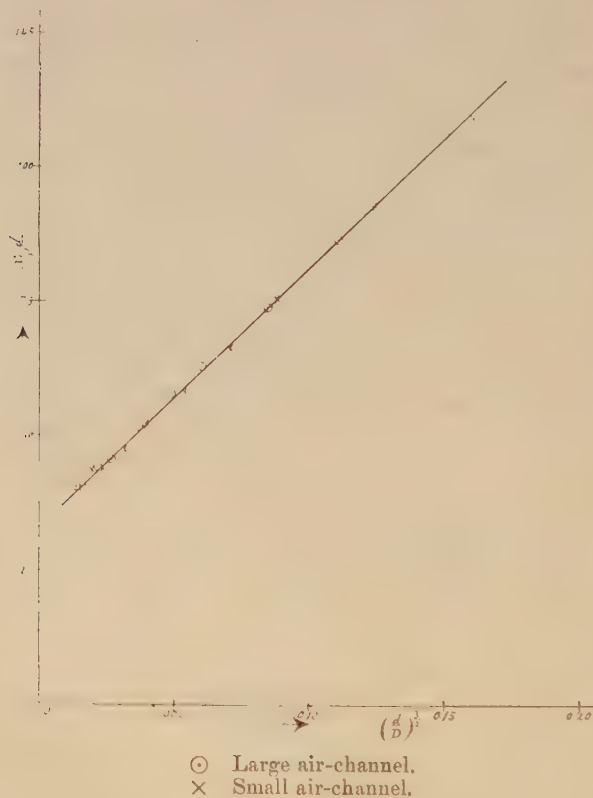
B. Cylinders.

Nine cylinders of various diameters (1.46 mm. to 5.94 mm.) and 3.2 cm. length were carefully turned on a lathe. A cylinder was supported vertically and symmetrically across the air channel (which was horizontal). The motion was considered as being nearly two-dimensional—at least in the middle of the vessel. The same formula as for a sphere was found to be applicable, as shown in fig. 2; the values of A_1 and A_2 being 2.65 and 48.2 respectively.

It was more difficult to get the two sets of eddies symmetrical in this case. No periodic eddying motion was

observed, such as has been obtained by Kármán and Rubach, Nayler and Frazer, and others. The maximum value of $\frac{vd\rho}{\mu}$ which we could reach was, however, only 50, and

Fig. 2.—Cylinder.



measurements were difficult before this value was reached. The value at which it was obtained in the case of the last pair of observers was 150.

C. Plates.

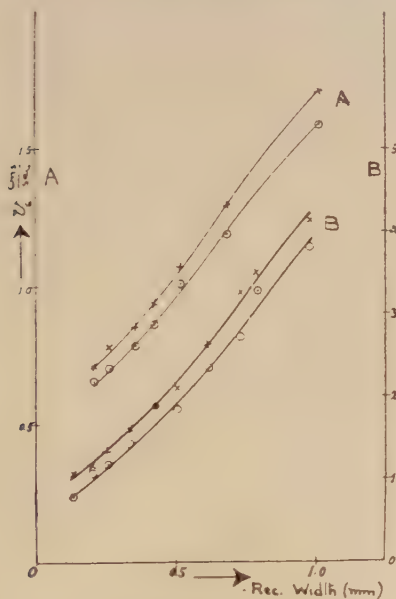
It is clear that the case of plate obstacles is not so simple as the others, because even if they be treated as infinitely long there are both the breadth and the thickness to take into account. Moreover, the indefinite sharpness of the edges introduces additional complication. The usual simple theory which allows infinite velocity at a sharp edge gives us no help.

The experiments were carried out (a) with plates of various widths but of constant thickness; (b) with plates of various thicknesses but constant width; and (c) with plates for which the thickness was in the same ratio to their width. The specimens were made of watch-spring when the thickness was small; in other cases they were brass or zinc plates. In each case the plate was placed with its length perpendicular to the air-current, the final testing being made by an examination of the degree of symmetry of the eddies.

(a) *Plates of constant thickness.*

Two sets were examined. In one set the thickness was 0.15 mm. and in the other 1.62 mm. The range of width in

Fig. 3.—Plates of equal thickness.



- Large air-channel.
- × Small air-channel.
- A Thickness = 0.15 mm.
- B Thickness = 1.62 mm.

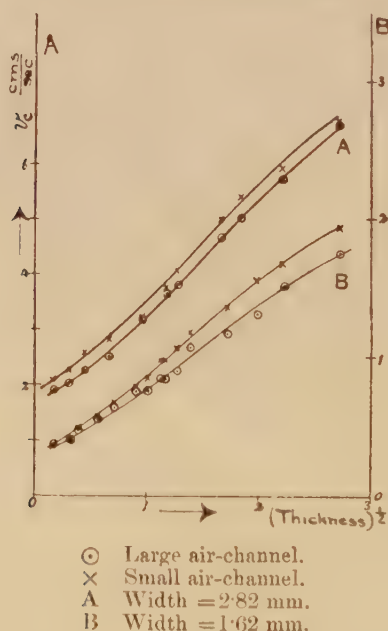
the former set was from 1 mm. to 5 mm.; in the latter set from 1 mm. to 7.5 mm. A small correction was applied by the method of successive approximation on account of small differences in the approximately constant thickness. All the observations were reduced to 20° C. If we plot the critical velocities against the reciprocal of the width, two nearly parallel straight lines are obtained which correspond to the two air-channels, as shown in the curves A and B on fig. 3.

The curve A is for the thinner plate. There is a tendency for the values to become constant when the width decreases, and further, it would seem that the critical velocities do not tend to zero however great the width becomes.

(b) *Plates of the same width.*

Two sets of plates were studied; in one set the width was 1.52 mm., and the thickness varied from 0.03 mm. to 7.5 mm.; in the second set the width was 2.82 mm., and the thickness varied from 0.03 mm. to 9.5 mm. Plotting the critical velocities against the square roots of the thickness, the curves A and B (fig. 4) are obtained for the 2.82 mm.

Fig. 4.—Plates of same width.



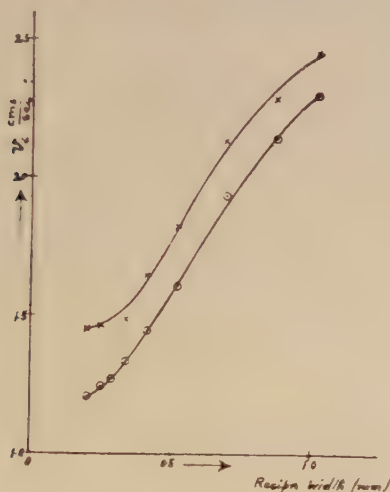
and 1.62 mm. widths respectively. There is a tendency to approach to constant values as the thickness increases. No effects of vibration were observed, although some of the plates were very thin.

(c) *Constant ratio plates.*

The constant ratio of thickness to width was $1/2$, while the thickness varied from 0.5 mm. to 2.5 mm. The curves

on fig. 5 represent the critical velocities plotted against the reciprocals of the widths. Simple power laws do not appear to be valid over the whole range, but we may state that the critical velocity changes with the square root of the thickness and the reciprocal of the width as long as the dimensions of the plate are moderate compared with that of the air-channel.

Fig. 5.—Constant ratio plates.



○ Large air-channel.

× Small air-channel.

Experiments were also made in a few cases for which the section was not rectangular. A trapezoidal cylinder was taken of which the parallel sides had widths of 2 mm. and 3 mm. respectively. The air-current was incident alternately on the wide and on the narrow side; in the former case the critical velocity was 1.9 times the value for the second case. Again, in the case where the cylinder had a triangular section, when the air flows from the apical line to the corresponding base the critical velocity is about four times larger than in the case of reversed flow.

The following general remarks should be made:—

(1) There was special difficulty in fixing the precise value of the critical velocity, both when the obstacles are very large and very small.

(2) The viscosity and the temperature coefficient for the mixture of air and smoke was taken as being the same as for air.

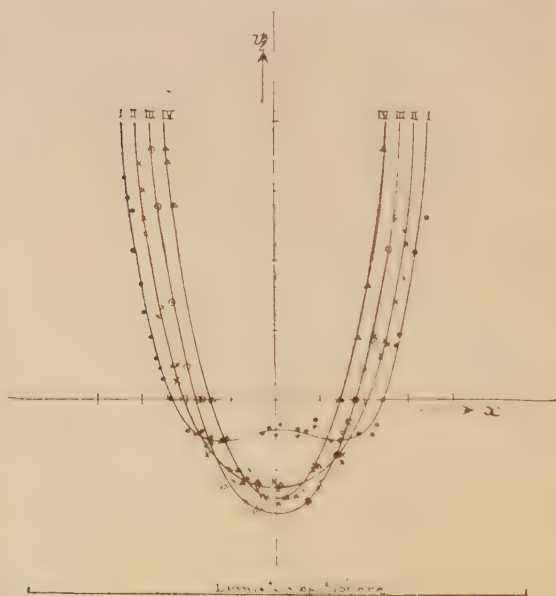
(3) The observation windows in the air-channel would have some effect. The length of the channel is also not without influence, as was shown by making a few determinations with a very short channel. In the actual experiments the channel was long enough for the eddies formed at the inlet to subside. This was tested by taking a photograph without an obstacle—the smoke streaks indicated that the velocity was practically constant and uniform in the neighbourhood of the axis of the channel.

PART II.

This part of the paper deals with the velocity distribution in the eddies when they are formed.

Several methods have been used to study this distribution. By using a magnesia cloud obtained by burning magnesium ribbon instead of tobacco smoke * and a full aperture lens,

Fig. 6.—Sphere (longitudinal components).



the field was bright enough to take “instantaneous” photographs of the particles. This was done after suitable steady eddies had been obtained by modifying the velocity

* Ammonium chloride was also tried, but it settles on the obstacle and on the walls of the channel.

of the current. Each magnesia particle is represented on the photograph by a line whose direction and length represent the direction and magnitude of the velocity in the corresponding region of the eddy. The duration of the exposure was varied from $\frac{1}{5}$ to $\frac{1}{20}$ second, depending upon the velocity of the stream. Since a high velocity is needed to produce eddies with small obstacles, the investigation was restricted to the medium-sized obstacles.

In order to measure the photographs obtained, each of them was placed in a lantern in turn and a magnified

Fig. 7.—Sphere (transverse components).

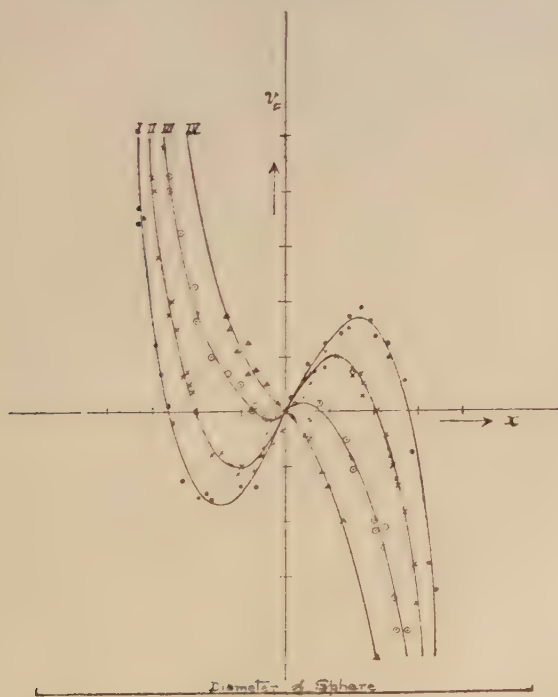
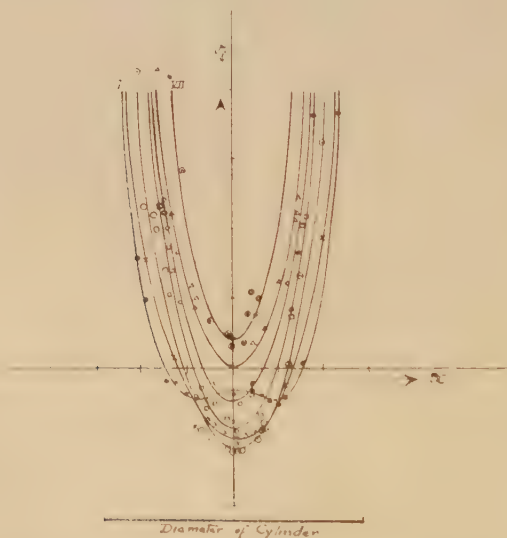


image (about 30 times magnification) was projected upon squared paper. The rectangular components of the streaks were then measured, and thus the longitudinal and transverse velocity components in the eddy were obtained. Each of these components was then plotted (in separate diagrams) against the position in the eddy to which it corresponds, the position of the obstacle, the centres of the eddies, and the neutral point (on the axial line) being used as reference

marks. The curves I, II, III, IV in fig. 6 and fig. 7 represent the longitudinal and transverse components of the velocities corresponding to the sections I, II, III, IV shown in photograph A, reproduced in fig. 8 (Pl. XII.), for the case of a sphere 5.56 mm. diameter, the value of $\frac{rd\rho}{\mu}$ being 24.2, in

the larger air-channel. The curves represent the longitudinal components and all except I bear a resemblance to curves of the second degree. Curve I has a peculiarity near the axis consequent upon the existence of the "dead space." The values of x are distances measured from the axial line.

Fig. 9.—Cylinder (longitudinal components).



The curves I to VI in fig. 9 and fig. 10 express the longitudinal and transverse components of velocities in the corresponding sections of the photograph reproduced in fig. 11 (Pl. XII.), for the case of a cylinder of diameter 2.85 mm. in the small air-channel for a value of $\frac{rd\rho}{\mu} = 11.6$.

The curves I to VII in fig. 12 and fig. 13 show the distributions of the longitudinal and transverse components of

Fig. 10.—Cylinder (transverse components).

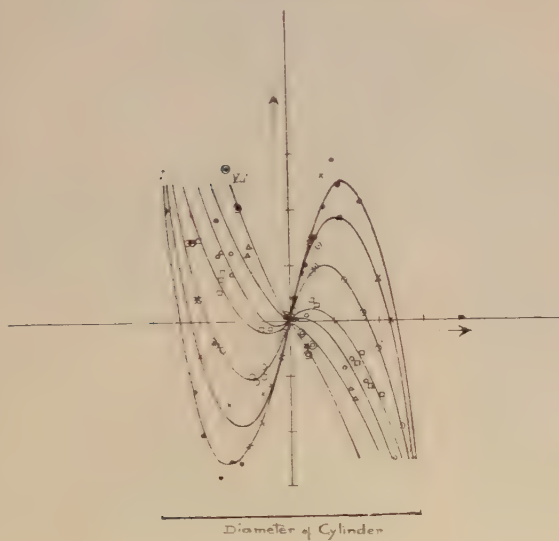


Fig. 12.—Plate (longitudinal components).

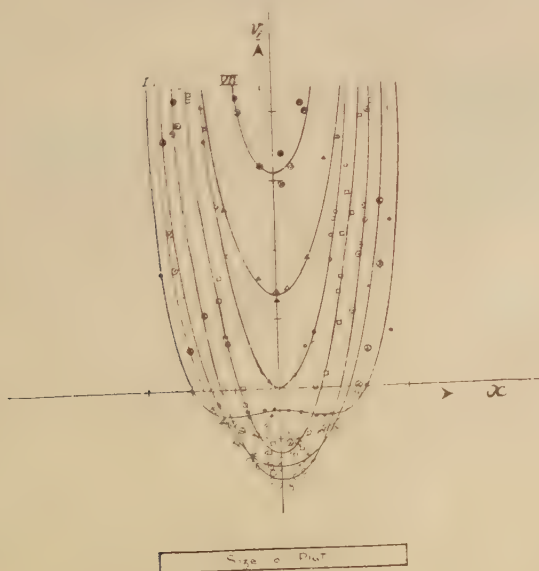


FIG. 8.

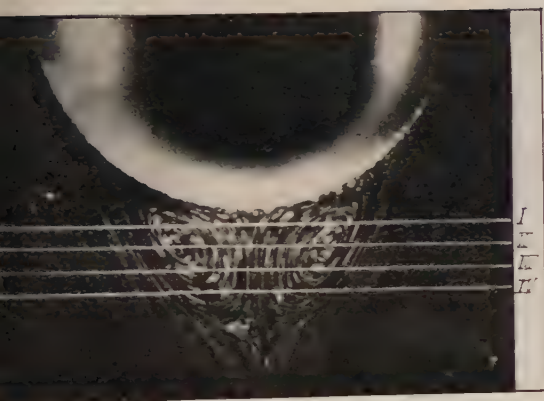


FIG. 11.



FIG. 14.

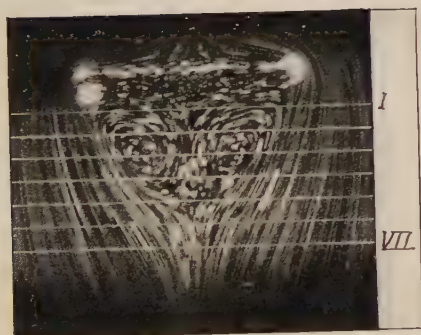
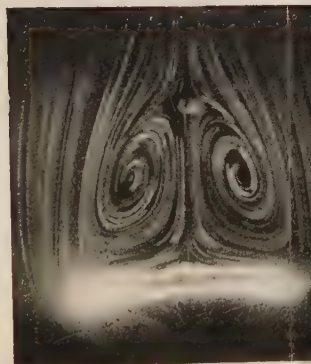


FIG. 15.



PART III.

Relation between the mean velocity and the position of the eddies.

The photographs of the eddies behind an obstacle were taken for different mean velocities; these images were projected on to squared paper and measured as before.

Fig. 16.

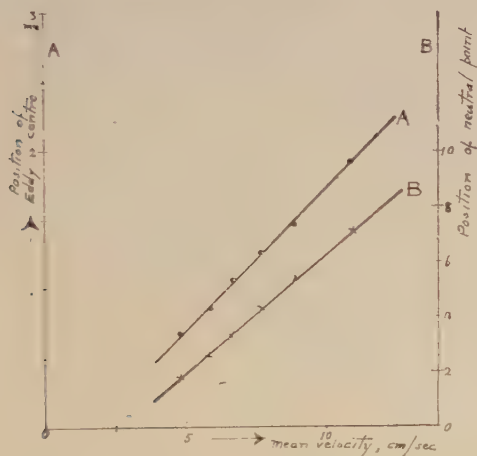
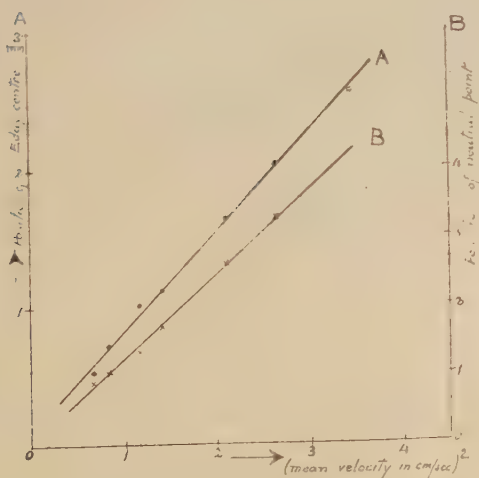


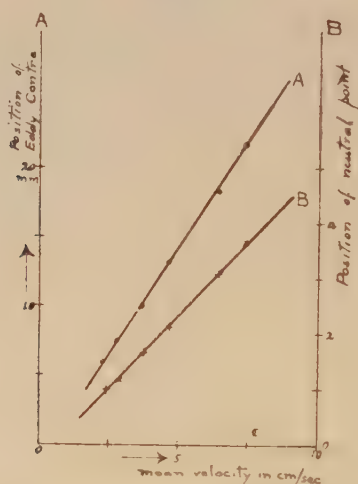
Fig. 17.



Relations are found between the motions of the centres of the eddies and of the neutral point when plotted against the mean velocities, as shown in fig. 16 for a sphere, and on fig. 17,

when plotted against the square of the mean velocity, for a cylinder. The locus of the centres of the eddies is not expressible by the formula which was given by Föppl, but the boundaries were not the same as in his case. The distance of the centres is found to be nearly proportional to the square of the mean velocity.

Fig. 18.



In fig. 18 are shown the corresponding data for a square sectional plate (2.8×2.8 mm.). It was expected that this would approximate to the case of a cylinder. It was found, however, that both for this plate and for a thin plate (2.8 mm. \times 0.2 mm.) the distances are proportional to the mean velocity itself.

LXXXVII. *The Distribution of Velocities among the Electrons emitted by Hot Platinum in an Atmosphere of Hydrogen.*
By HAROLD H. POTTER *.

Part I.—CONSIDERATIONS OF A GENERAL CHARACTER.

Introduction.

THE first measurements on the energy distribution among the electrons emitted by hot metals were made by Prof. O. W. Richardson and F. C. Brown †, and by O. W. Richardson ‡. Both the normal and the tangential components

* Communicated by Prof. O. W. Richardson, F.R.S.

† Phil. Mag. xvi. p. 353 (1908).

‡ Phil. Mag. xvi. p. 890 (1908); xviii. p. 681 (1909).

of the velocity were studied, and the experiments showed that the distribution of energy among the electrons emitted by platinum in air at low pressures was in close agreement with Maxwell's Distribution Law for a gas of molecular weight equal to that of the electrons in thermal equilibrium at the temperature of the hot platinum. Some experiments were also made on lime-coated filaments and on platinum filaments in an atmosphere of hydrogen. In both cases the velocity distribution did not appear to be in agreement with Maxwell's law. The experiments on lime-coated filaments seemed to give fairly definite results, but in the case of hydrogen—to quote the authors—"the results were too irregular to draw very definite conclusions from." The present series of experiments were undertaken in the hope of clearing up some of these points.

The experiments of Richardson and Brown were carried out with plane parallel electrodes. Schottky *, later, measured the velocity distribution among the electrons emitted by carbon and tungsten filaments surrounded by cylindrical electrodes. Schottky found that although the linear relation between the logarithm of the current and the retarding voltage held good, the average energy of the electrons was greater than demanded by theory.

In 1917 further experiments on platinum and tungsten were made in this laboratory by Mr. Sih Ling Ting †, using the cylindrical anode method, and the results appeared to confirm the view that the average energy was greater than that demanded by Maxwell's law. The whole question has been recently re-examined at the instigation of Prof. Richardson by J. H. Jones ‡, who has shown that in the case of tungsten, Maxwell's law is satisfied both as regards the linear relation between the logarithm of the current and the voltage and as regards the value of the average energy. The high energy values of Ting have been shown to be due to faulty circuit arrangements. Similar conclusions have recently been reached by L. H. Germer § and in the present paper. There is no longer any doubt but that the electrons emitted from a clean metal surface *in vacuo* possess a Maxwell velocity distribution.

* *Ann. d. Phys.* xlv. p. 1011 (1914).

† *Proc. Roy. Soc. A*, xcviii. (1221).

‡ *Proc. Roy. Soc. A*, cii. p. 734 (1923).

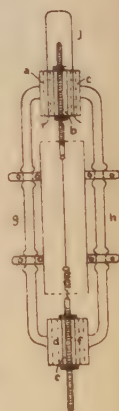
§ 'Science,' lvii. p. 392 (1923).

Description of Apparatus.

The apparatus and electrical connexions were practically the same as the second arrangement used by Dr. Jones in his investigation of the energy distribution of the electrons emitted by hot tungsten (Jones, *loc. cit.* fig. 8, p. 744).

The construction and the mountings of the thermionic tube are shown in figs. 1 and 2. The cylinder and the filament were mounted on a quartz frame, as shown in fig. 1. *a, b, c, d, e, f* are six pieces of quartz capillary tubing 16 mm. long and 1.5 mm. internal diameter, made together in groups of three and fixed by quartz rods *g* and *h* so that the tubes *a, b, c* are directly opposite the tubes *d, e, f*. The filament was secured at one end to a copper rod and at the other end to a molybdenum spring, which in its turn was fastened to a second copper rod. The copper rods were threaded, and held in position in the tubes *b* and *e* by four small nuts. The cylinder was secured to the quartz frame by riveted copper bands, as shown. *j* is a hook, used to support the quartz frame inside the exhausted tube.

Fig. 1.



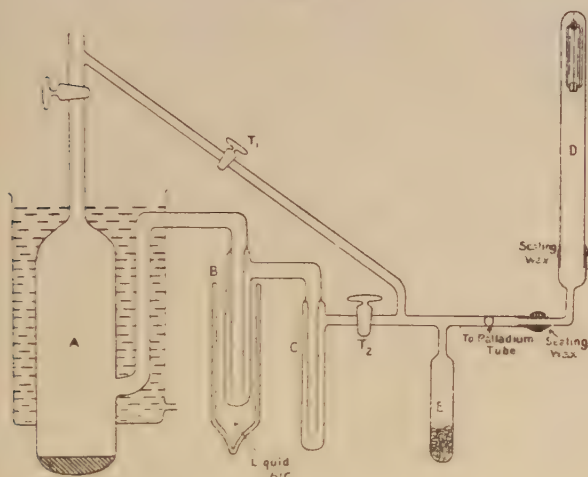
This quartz frame, which had been used previously by Dr. Jones for other work, was admirably suited for use in this experiment. One of the principal points in mind in designing the apparatus was to obtain an arrangement in which the filament could be replaced easily. The high volatility of platinum makes it well-nigh impossible to work with any one filament for a long period, and consequently it was important to be able to replace filaments easily and quickly. This condition is evidently fulfilled by the quartz frame arrangement, the removal of the filament being merely a matter of unscrewing a few nuts. The containing quartz tube was also designed with the same object in view. It consisted of a tube 33 cm. long and 4 cm. internal diameter, fitted with a cap with suitable outlets for electric leads and exhaust. The cap was fixed with sealing-wax, and the exits for the electric leads were also secured with sealing-wax. The tube was fixed in a vertical position with the cap at the lower end. In the upper end of the tube was a quartz hook which served to support the quartz frame, etc.

Pumps, etc.

The exhausting of the tube was carried out by means of a mercury vapour diffusion pump backed by a Gaede and an oil pump.

The connexions between the diffusion pump A and the tube are shown in fig. 2. The diffusion pump A was connected through two liquid-air traps B and C (used to keep the mercury vapour out of the quartz tube) to the quartz tube D. E is a charcoal tube which can be surrounded by liquid air. A tube was provided to short-circuit the diffusion

Fig. 2.



pump so that air could be let into the quartz tube and subsequently pumped out without admitting air to the diffusion pump. When the diffusion pump was being used the tap T_1 was of course closed. Hydrogen could be admitted to the apparatus by means of a palladium tube.

Cleaning up of Quartz Tube and Electrodes.

The object of using quartz apparatus was to facilitate the cleaning-up process. With glass it is extremely difficult to get rid of the occluded gases, and it is impossible without the aid of a vacuum furnace to raise a glass tube to a sufficiently high temperature to clean up the metal inside. In these experiments the tube was heated by means of an electric furnace at a temperature of about 1000 °C.

for two or three hours, a vacuum being maintained meanwhile by the working of the mercury vapour pump. The rapid evolution of gas by the various parts of the apparatus at these high temperatures made it impossible to maintain a high vacuum, but the mercury diffusion pump was so rapid in its working that the pressure after the first few minutes' heating rarely rose above $\frac{1}{1000}$ mm. of mercury. The speed of the pump is of some importance in another respect. It is well known that at high temperatures quartz is permeable to hydrogen. At the high temperature of the electric furnace the dissociation of water vapour is sufficiently high for hydrogen to have been present in appreciable quantities outside the quartz tube, but any, however, which found its way through the quartz would have been removed too quickly to exert any "permanent" effect on the platinum filament.

With the method of cleaning up described the copper becomes very bright and clean.

This intense heating made it necessary to use a long tube, so that all sealing-wax joints were a long way from the furnace. Heat reached the sealing-wax chiefly by radiation through the evacuated tube and by conduction along the electrical leads. It was found impossible, using a tube 16 cm. long, to keep the sealing-wax hard even with water cooling, but with the long tube described above the joints could be kept quite hard with the help of occasional blasts of cold air.

After heating in the furnace, the tube was allowed to cool gradually, the filament being glowed during the cooling at about 1500° C. This caused a temporary emission of gas by the filament, and at the same time prevented condensation on the filament of any vapours present in the tube.

PART II.—EXPERIMENTS ON THE VELOCITY DISTRIBUTION.

Theoretical Considerations.

Assuming that the distribution of velocities among the emitted electrons is in accordance with Maxwell's law, the current i flowing between two parallel plates under a potential difference V is given by

$$i = i_0 e^{-\frac{Ve}{kT}}, \quad \dots \dots \dots (1)$$

$$\text{or} \quad \log \frac{i}{i_0} = -\frac{Ve}{kT},$$

where i_0 is the saturation current, k Boltzmann's constant,

T the absolute temperature of the emitting electrode, and ϵ the electronic charge. The average kinetic energy of the stream of electrons is $2kT$.

Schottky has shown that for cylindrical electrodes the expression is

$$\iota = \iota_0 \sqrt{\frac{2}{\pi}} \left\{ x e^{-x^2} + \int_x^\infty e^{-x^2} dx \right\}, \quad \dots (2)$$

where $x = \sqrt{\frac{V\epsilon}{kT}}$, provided the radius of the anode is sufficiently large in comparison with the radius of the wire.

Plotting V against $\log_{10} \frac{\iota}{\iota_0}$, we get, according to equation (1),

a straight line given by the equation $\log_{10} \frac{\iota}{\iota_0} = -\cdot4343x^2$.

Except near $x=0$, equation (2) gives a straight-line relation given by $\log_{10} \frac{\iota}{\iota_0} = -\cdot405x^2$,

$$\text{or} \quad \log_{10} \frac{\iota}{\iota_0} = -\cdot405 \frac{V\epsilon}{kT} = -\cdot405 \frac{V\nu\epsilon}{RT},$$

where ν = number of molecules in 1 c.c. of a perfect gas at 0°C . and 760 mm. pressure, and R is the constant in the equation $p\nu = RT$ calculated for the stated quantity of gas.

The difference in equations (1) and (2) has been shown graphically by Schottky* and Ting†:

$$\nu\epsilon = -\cdot4327 \text{ e.m. units,}$$

$$R = 3\cdot711 \text{ ergs/degs. centigrade.}$$

Thus, if V is in volts,

$$\log_{10} \frac{\iota}{\iota_0} = \frac{4720V}{T}.$$

Thus the slope of the $(\log_{10} \frac{\iota}{\iota_0}, V)$ curve is inversely proportional to the temperature and to the average energy of the electron stream. One obviously arrives at the same value of the slope by plotting $\log \iota$ against V . Further, the units in which ι is measured do not affect the slope. In the results given in the graphs below, ι has been given in terms of the galvanometer deflexion.

* *Ann. d. Phys.* xliv. p. 1018 (1914).

† *Proc. Roy. Soc. A*, xeviii. p. 378.

Owing also to the presence in the tube of a contact potential, it was difficult to tell the exact value of the retarding or accelerating voltage; but this does not constitute a real difficulty, as it is only necessary, in order to obtain the slope of the ($\log i, V$) curves, to note the change in the current produced by a given increment in the voltage. The voltage shown in the graphs is that registered by the voltmeter.

Method of Experimenting.

The main object of this part of the work was to obtain a clean platinum filament which had not been heated in hydrogen, to measure the slope of the ($\log i, V$) curve at a definite temperature, and then to admit hydrogen to the apparatus and again measure the slope at the same temperature.

Temperature of Filament.

An accurate knowledge of the actual temperature of the filament was not necessary in these experiments, but a rough estimate from pyrometric and resistance measurements gave about 1450°C . as the temperature at which nearly all these experiments were made. It was found advisable not to go much above this temperature, as the volatility of the platinum was so high that the filaments soon fused.

In order to keep the filaments at a constant temperature, the resistance was kept at a constant multiple of the resistance at room temperature. This was the method used by H. A. Wilson to keep the temperature of the filament the same in high vacuum and in hydrogen.

Phenomena connected with cleaning up of Filament.

Various methods of cleaning up the filament have been used by other experimenters. H. A. Wilson in his work used nitric acid, but this may contaminate the surface with an oxide. Lockrow suggests alternate heating of the filament in hydrogen and oxygen. The writer has found this method very successful, but on the other hand it does not seem desirable in experiments designed to show the effect of hydrogen on the emission from platinum to first of all clean up the platinum by heating it in hydrogen. The method adopted in this experiment was to clean up the wire entirely by heating in high vacuum at a high temperature. Herein lay the greatest difficulty of the experiment. The melting-point of platinum is low and its volatility high, so that it was

difficult to remove the more refractory impurities. In fact, a large proportion of the filaments fused before the impurities had been driven off. However, by the exercise of a sufficient amount of patience, a considerable number of filaments have been found to give satisfactory results.

After the heating in the furnace and the driving of gas from the filament described above, a high vacuum was produced by the diffusion pump, and then the taps T_1 T_2 (fig. 2) were closed and liquid air applied to the charcoal tube. In general the electron emission was at first very small, but after a few hours' glowing of the filament it began to grow. On the other hand, the initial currents were sometimes abnormally high—due perhaps to the presence on the wire of substances such as lime, which have a high electron emissivity. Occasionally the cleaning-up process was complete in about three hours, but usually took anything up to twenty-four hours, and sometimes as much as sixty hours.

The best criteria of the wire being clean appear to be the stability of the emission and the shapes of the current potential curves. If the filament is clean the emission readily saturates, but if it is dirty it is very difficult to get saturation, owing probably to the existence of local fields at the surface of the wire.

Results.

In all experiments which have been made, the linear relation between the logarithm of the current and the voltage has been found to hold good at low values of the current. For higher values of the voltage, the current was found to increase less rapidly with the voltage than would satisfy a linear relation. This is exactly as demanded by theory.

Experiment 1.—Tube heated $2\frac{1}{2}$ hours in furnace, and filament subsequently heated for 3 hours in high vacuum.

Four curves similar to fig. 3, showing current potential relations in high vacuum, gave slopes of the log curves equal to 2.70, 2.53, 2.90, and 2.60. Mean = 2.68.

Experiment 2.—No heating of tube in furnace, as copper anode and tube were already very clean. Filament glowed 24 hours in high vacuum.

Measurements were made in hydrogen at a pressure of 0.25 mm. Three curves similar to fig. 4 gave slopes of the log curves equal to 2.05 and 1.95 respectively. The slope of the log curve for emission *in vacuo* was 2.5.

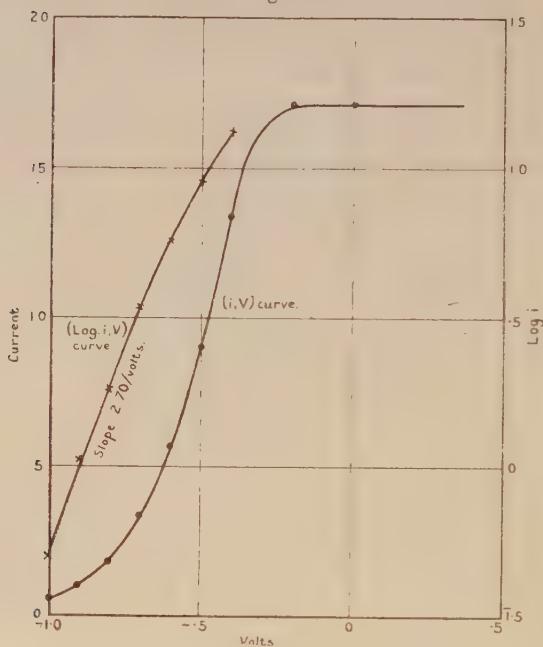
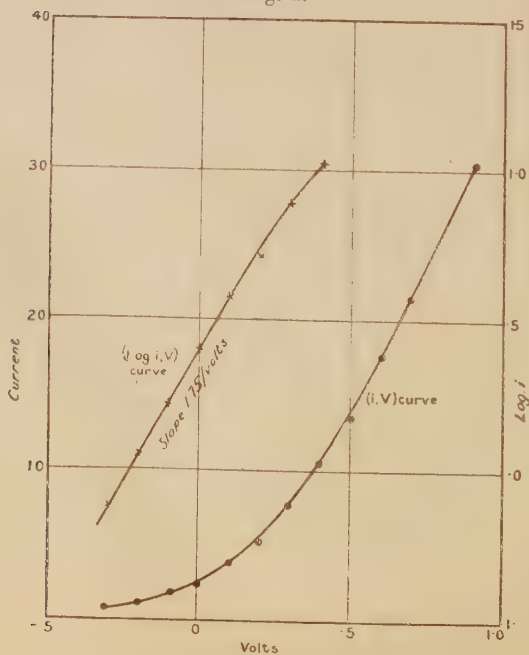


Fig. 4.



Experiment 3.—Tube heated in electric furnace for 2 hours, and filament subsequently heated in high vacuum for 2 hours.

Three curves showing current voltage relations were obtained. Two gave slopes of 2.65 and 2.75 in high vacuum; the other was obtained with a pressure of hydrogen = $\frac{165}{1000}$ mm. and gave a slope = 1.75.

Experiment 4.—Two hours' heating in electric furnace followed by alternate heating of filament in hydrogen and air.

The results of this group of experiments in the order in which they were made are as follows:—

Slope of log curve.	Pressure of Hydrogen (mm. $\times 10^{-3}$).
2.78	0
2.60	0
2.82	0
2.52	15
2.60	40
1.75	175
1.75	70
1.61	54
2.55	22
1.90	140
2.90	0
1.50	145
2.75	0
2.40	400

Experiment 5.—Tube heated 2 hours in furnace, and filament subsequently glowed alternately in hydrogen and high vacuum.

Two curves were obtained, showing a slope of 2.46 for curve obtained *in vacuo* and 1.31 in hydrogen at .30 mm.

Discussion of Results.

The five series of results given above show clearly that for pressures of hydrogen greater than $\frac{50}{1000}$ mm. the slope of the ($\log i, V$) curve is less than in vacuum.

A mean of thirteen experiments in high vacuum gave 2.68 volts as the slope of the ($\log i, V$) curves. The slope demanded by theory, if Maxwell's law is obeyed, is 2.72 at a temperature of 1450° C.

In the presence of hydrogen the linear relation between $\log i$ and V has been found to hold, but the slopes of the various curves have very low values. The mean of thirteen measured values of the slope at various pressures of hydrogen is 1.96. The writer has been unable to find any relation

between the pressure of the gas and the slope of the curve. Slopes as high as 2.40 have been measured at a pressure of $\frac{400}{1000}$ mm. of hydrogen, and as low as 1.31 at $\frac{300}{1000}$ mm. and 1.61 at $\frac{51}{1000}$ mm. The previous treatment of the wire is undoubtedly of importance, and the effect is of a semi-permanent nature. With increasing pressures of hydrogen the slope does not at first appear to decrease very much, but if a low slope has once been obtained and the gas is then pumped out, the slope remains low until a fairly small pressure has been obtained, when it will suddenly increase. This is shown in readings 1 to 9, Experiment 4.

The effect is undoubtedly of a complicated nature, and in the absence of further evidence it is impossible to say exactly on what conditions the low slope depends. The one fact, however, remains that with five different specimens of platinum the slope of the $(\log i, V)$ curves has without a single exception been found to be abnormally low for pressures of hydrogen above $\frac{1}{20}$ mm. These low slopes may arise in two ways:

1. Through the agency of local fields at the surface of the filament.

2. By an actual increase in the energy of the electrons.

The writer has measured the slope of the $(\log i, V)$ curves for a tungsten filament, sputtered with thorium, in which these local fields are supposed to exist. It has been found that the slope of these curves is considerably below that required by Maxwell's law.

One of the requirements of the local field theory, however, is apparently that the current-potential curves should not easily saturate. This is known to be so in the case of thorium-sputtered filaments, but the writer has found no evidence to support this explanation of the low slopes of the curves from platinum. Fig. 5 shows one of these low-slope curves, and fig. 6 shows the same curve on a different scale for potentials up to 8 volts. The saturation is seen to be almost perfect and to be complete at zero voltage.

The low slopes cannot be occasioned by the shortness of the mean free path, as there seems to be no theoretical reason why elastic collisions should affect the energy distribution. Further, F. C. Brown* has shown that the energy distribution amongst the positive ions emitted from platinum is independent of the gas- (air) pressure from

* Phil. Mag. xvii. p. 355 (1909).

·009 mm. to 28·0 mm.—a very much greater range than has been used in the writer's experiments. Also any effect due to collisions would be expected to be some regular function of the gas-pressure. We are led, therefore, to conclude that the average energy of the electrons emitted from platinum, as measured by this method, is higher in an atmosphere of hydrogen than in vacuum. Exactly how this may be brought about is not readily explained. Prof. Richardson has made

Fig. 5.

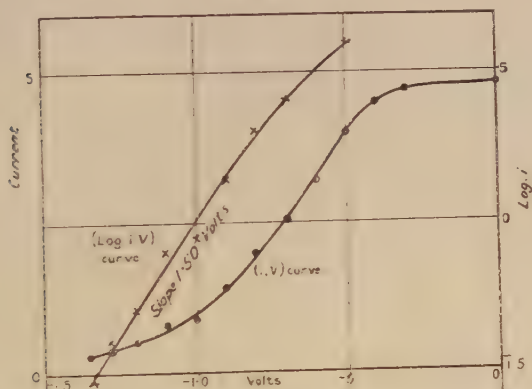
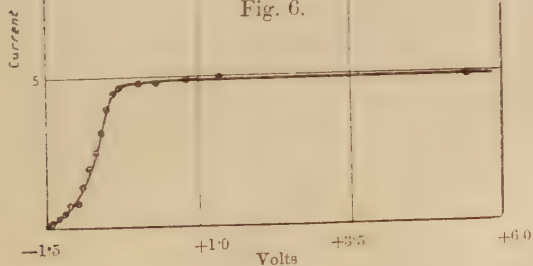


Fig. 6.



two suggestions—(1) that owing to the presence of the hydrogen the surface of the wire is in a state of polarization, and that the electrons are consequently emitted with a velocity above the normal; (2) that the electrons may start with a Maxwell distribution which is subsequently modified by local fields of force, thus giving rise to the abnormal measured values. This seems to be excluded if easy saturation can be considered as a reliable test for the absence of local fields. We cannot, however, be sure that it is.

Part III.—SOME EXPERIMENTS ON THE EFFECT OF HYDROGEN ON THE TOTAL EMISSION FROM PLATINUM.

In 1904, H. A. Wilson * came to the conclusion that the emission of electrons from hot platinum was greatly increased in the presence of hydrogen. This became the subject of a number of researches by O. W. Richardson †, F. Horton ‡, G. H. Martyn §, Lockrow ||, among others.

The results of these researches were of a complicated nature, but the main points were as follows :—

With “new” wires (*i.e.*, wires which have not been subjected to prolonged heating in hydrogen) the emission at a given temperature was increased on admitting hydrogen to the apparatus. “Old” wires were found to give an emission independent of the pressure of hydrogen.

In view of the effect of hydrogen on the average energy, it is interesting to examine the effect on the total emission under the same conditions. The experiments described in this section were carried out with the same filaments and at the same time as the experiments on the velocity distribution described above.

Results.

In the results given below, the values of the saturation currents from five different samples of platinum are given for vacuum and for various pressures of hydrogen. The currents are given in terms of galvanometer scale deflexions. The sensitivity of the galvanometer was 1 cm. deflexion for 3×10^{-9} amp. The thermionic circuit was “made” for about $\frac{3}{4}$ of the total time, so that 1 cm. deflexion represented a current of 8×10^{-9} amp. The diameter of the filaments was .05 mm. and the length about 3.5 cm., so that a deflexion of 1 cm. represented a current density of 7×10^{-8} amp. per sq. cm.

1st Experiment.—Same wire as Experiment 1, Part II.

Tube heated $2\frac{1}{2}$ hours in furnace, and filament subsequently heated for 3 hours in high vacuum.

Sat. current (cm. scale divisions).	Pressure of hydrogen (mm. $\times 10^{-3}$).
17.10	0
18.00	0
13.70	0
14.10	0
12.00	200
13.00	0
18.60	0

* Phil. Trans. A, ccii. p. 243 (1904); Phil. Trans. A, ccviii. p. 247 (1908); Proc. Roy. Soc. A, lxxxii. p. 71 (1909).

† Phil. Trans. A, ccvii. p. 1 (1906).

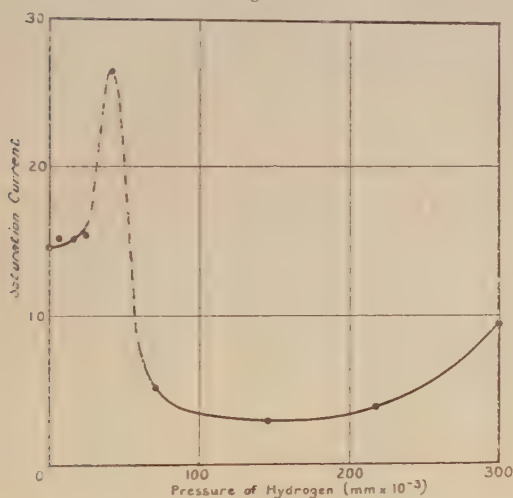
‡ Phil. Trans. A, ccvii. p. 149 (1908).

§ Phil. Mag. (6) xiv. p. 306 (1907). || Phys. Rev. p. 97, Feb. 1922.

After further prolonged heating of filament in high vacuum :—

Sat. current (cm. scale divisions).	Pressure of hydrogen (mm. $\times 10^{-3}$).
8.00	0
10.80	250
9.80	150
10.00	90
9.80	50

Fig. 7.



After this series of figures was taken, some air was let into the apparatus. The emission fell off at once to something too small to be measured with the galvanometer. Pumping out the air and admitting hydrogen immediately restored the emission to its former value.

2nd Experiment.—Same filament as in Experiment 2, Part II.

No heating in furnace as copper anode and tube were clean. Filament glowed about 24 hours in high vacuum.

Saturation current (cm. scale divisions).	Pressure of hydrogen (mm. $\times 10^{-3}$).
13.70	250
10.15	0
11.75	250
11.75	0

3rd Experiment.—Same filament as in Experiment 3, Part II.

Two hours' heating in electric furnace and 2 hours' glowing of filament in high vacuum.

Saturation current (cm. scale divisions).	Pressure of hydrogen (mm. $\times 10^{-3}$).
33.70	0
35.00	350
36.4	0
25.8	175
53.0 (?)	165

4th Experiment.— $1\frac{1}{2}$ hours' heating in furnace. Filament glowed for 60 hours in high vacuum.

Saturation current (cm. scale divisions).	Pressure of hydrogen (mm. $\times 10^{-3}$).
15.05	0
16.00	260
13.00	8
9.00	125

5th Experiment.—Same filament as in Experiment 4, Part II.

Two hours' heating in electric furnace followed by alternate heating of filament in hydrogen and air.

Saturation current (cm. scale divisions).	Pressure of hydrogen (mm. $\times 10^{-3}$).
9.35	0
7.80	100
7.80	0
7.30	0
20.50	15
27.10	40
10.30	175
6.50	70
5.60	54
19.50	22
6.80	140
16.90	0
10.50	0
5.25	145
12.60	0
14.55	0
14.60	400
17.90	0

Discussion of Results.

The five sets of results tabulated above were obtained with five different specimens of platinum. In each of the first four groups the wire was cleaned by heating for a prolonged period in high vacuum. There was little or no indication of any increase in the emission from the filament when hydrogen was introduced into the tube. The one case where an appreciable increase was noticed (the last reading of Experiment 3) may be explained as follows:—The filament

fused soon after this reading was taken, which means that one part of the wire had got very hot, and so was emitting strongly. It is quite likely for this to happen in spite of the total resistance of the wire being kept constant by control of the heating current. Apart from this one instance, there are no changes in the emission which could not be attributed to changes of temperature.

The fifth group of experiments in which the wire was cleaned by alternate heating in hydrogen and oxygen gave results of a somewhat different nature. The inference from this series of results would be that for pressures of hydrogen below $\frac{1}{20}$ mm. the emission was somewhat greater than in a vacuum, but for the pressures above this value it was less. This set of readings does not, however, appear to be as reliable as the four preceding sets, the vacuum currents varying from 5.25 cm. to 17.90 cm.

Some Peculiar Phenomena observed during the above Experiments.

Two distinct kinds of phenomena have been observed under what appeared to be identical conditions.

1. A platinum filament which had been thoroughly cleaned by prolonged heating in high vacuum was found to give exactly the same emission after admitting hydrogen as it gave in high vacuum. On pumping out the hydrogen, however, the emission gradually decreased in a manner which made it roughly proportional to the pressure of the gas. At a pressure of $\frac{1}{10,000}$ mm. (the limit of the Gaede pump) the emission was practically zero. It could, however, be restored (a) immediately by admitting hydrogen, (b) gradually by applying liquid air to the charcoal tube and glowing the filament at about 1450° C. The phenomenon occurred with two different wires, and could be repeated almost indefinitely with either wire.

2. A phenomenon of somewhat different type was observed with other wires. Up to a point the phenomenon was the same as that described above, but on pumping out the hydrogen the emission decreased less quickly, and at a certain value of the pressure—always between $\frac{1}{20}$ mm. and $\frac{1}{100}$ mm.—the emission suddenly increased to about twice the vacuum value. With further reduction in the pressure the emission fell off steadily to the vacuum value. With increasing pressures of hydrogen the emission was not similarly affected. Further, if when the high emission was obtained the taps were closed so as to keep the pressure constant, the emission fell off gradually to the vacuum value.

These are only two of a large number of peculiar results obtained with platinum filaments in hydrogen, but these two have been mentioned because they have occurred so many times and with various samples of platinum.

The first peculiarity may be merely the result of a little air entering the tube when the taps were opened to start pumping out, but the effect was persistent even when the apparatus had been washed through several times with hydrogen. In the absence of further information, it is difficult to give any adequate explanation of the second effect mentioned. The effect is shown in fig. 7.

Relation between Average Energy and Total Emission.

There appears to be no relation between the measured average energy and the total emission from the filament: the energy was always increased on admitting hydrogen, whereas the effect on the total emission was quite small, any existing variation being sometimes in the direction of increasing current and sometimes in the reverse direction.

SUMMARY.

The electron emission from hot platinum has been measured in vacuum and in an atmosphere of hydrogen. The presence of hydrogen at pressures of $\frac{1}{2}$ mm. and over has been found to greatly affect the measured average energy of the emitted electrons.

Maxwell's Distribution Law has been found to hold for the emission from pure platinum in a high vacuum. The linear relation between the logarithm of the current and the applied voltage has been found to hold good in an atmosphere of hydrogen, but the average energy of the electrons has been found to be higher than that demanded by Maxwell's law. The average energy does not appear to be a regular function of the pressure.

Experiments on the total emission have indicated that if the platinum wire is quite clean hydrogen has little or no effect on the total emission at temperatures near 1450° C., but that the hydrogen has a considerable effect (usually increasing the emission) if the filament is contaminated (*cf.* Lockrow, *Phys. Rev.* p. 97, Feb. 1922).

I wish in conclusion to express my gratitude to Prof. Richardson for initiating these experiments, and for many valuable suggestions in carrying them out.

Physics Research Laboratories,
King's College, Strand.
October 1922.

LXXXVIII. *The Entrainment of Air by a Jet of Gas issuing from a Small Orifice in a Thin Plate.* By J. S. G. THOMAS, D.Sc. (Lond. and Wales), A.R.C.Sc., A.I.C., Senior Physicist, and E. V. EVANS, F.I.C., Chief Chemist, South Metropolitan Gas Company*.

Introduction.

IN a previous communication†, one of us has discussed the discharge of air at atmospheric temperature through a small orifice in a thin plate, and the entrainment of air by the jet of issuing gas. In the paper referred to the effects of size of orifice and of pressure at the orifice upon the discharge and air entrainment were more especially investigated. Recent developments within the gas industry, since the passing of the Gas Regulation Act, 1920, which conferred freedom upon individual gas undertakings to supply gas of any declared calorific value, have made a knowledge of the dependence of the air-entraining power of a gas jet upon various other factors extremely desirable. The efficient operation of any gas-burner of the Bunsen type depends primarily upon efficient air induction by the jet of gas issuing from the ejector of the burner. Towns' gas consists of a mixture of certain combustible constituents, viz., hydrogen, methane, ethane, carbon monoxide, and various unsaturated hydrocarbons, together with certain incombustible gases generally classified together as "inerts" and including nitrogen, oxygen, and carbon dioxide. The individual combustible constituents require various respective proportions of oxygen for their complete combustion. Thus while for this purpose hydrogen and carbon monoxide require only half their respective volumes of oxygen, methane requires twice and benzene vapour 7.5 times its volume of oxygen for complete combustion. The incombustible constituents generally are characterized by relatively high specific gravities compared with the combustibles, and it might, we think, be reasonably anticipated that, on this account, the degree of primary aeration of a jet of coal gas effected at any pressure would, *ceteris paribus*, be increased by an increase in the proportion of these "inert" incombustible constituents present in the gas. Under these conditions the designation "inert" would be a misnomer. Various other important practical considerations in connexion with

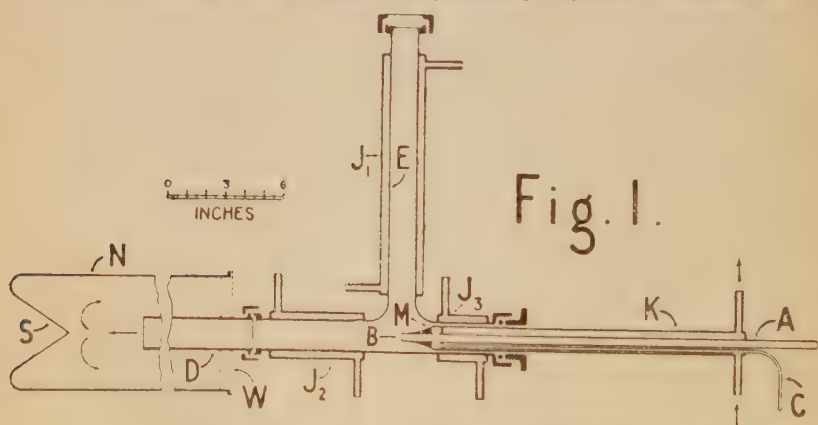
* Communicated by the Authors.

† Phil. Mag. vol. xliv. p. 969 (1922).

the subject have been summarized in the Ninth Report of the Joint Research Sub-Committee of the University of Leeds and the Institution of Gas Engineers to the latter body (1923). The subject of air entrainment in burners for use with varieties of towns' gas, of calorific values ranging from 3000 B.Th.U. to 600 B.Th.U. per cubic foot and of different specific gravities, has been discussed in recent papers issued by the Bureau of Standards, Washington*. We propose in the present paper to consider the dependence of air entrainment by a jet of gas upon the density of the gas in the jet and upon the density of the air into which the jet issues. Our experiments are confined to the gases, hydrogen, coal gas, air, and carbon dioxide.

Experimental.

The method of experiment corresponded very closely with that detailed in the previous communication†. In the present work, gases respectively lighter, heavier, and



of the same density as air were employed, and in order to eliminate as completely as possible any effect upon air entrainment arising from a vertical column of gas lighter or heavier than air, the discharge and air induction tubes were mounted horizontally. They are shown in plan in fig. 1 and differ slightly from those used in the previous work. The discharge tube A was provided with a jacket K, through which water, steam, or other heating fluid could be

* Technologic Papers, No. 193 (1921) and 222 (1922), U.S. Bureau of Standards, Washington.

† Phil. Mag. *loc. cit.* p. 973.

passed. The remaining tubes in the neighbourhood of the orifice B and for some distance therefrom were similarly provided with jackets, J_1 , J_2 , and J_3 , and the whole of the apparatus comprising the discharge and induction tubes carefully lagged with cotton wool and felt. The jacket J_1 was built in two sections each 15 inches long as shown. The orifice in the disk B was of such diameter that anomalous air entrainment such as that referred to in the previous work* did not occur within the range of pressures employed. The disk and orifice were carefully prepared from a nickel-steel sheet as previously detailed, and the disk was soldered to the discharge tube by means of hard solder. Pressure in the discharge tube at a point about 1.5 inches from the orifice was transmitted to a water manometer through a chamber M brazed to the discharge tube and connected with the tube C as shown. The pressure was read by a microscope to within 0.02 mm. Air supplied to the discharge tube was dried by passage over calcium chloride. A hot wire anemometer was inserted in the air induction tube E as previously described, to measure the volume of air entrained by the jet, and was arranged in such position that its indication was not affected by the temperature in the jacket J_1 . The mixture of gas discharged from the orifice and air induced by the jet was delivered into a comparatively large cylindrical vessel N provided with a re-entrant conical bottom as shown at S. The effect of external atmospheric disturbances on the jet was reduced to a minimum by providing the mouth of N with two layers of fine copper gauze W.

In the first series of experiments, dry air at a temperature of 14°C . (± 0.5) was discharged through the orifice and the volume of air entrained determined in the manner previously detailed†. In subsequent experiments, air was discharged through the orifice at temperatures of approximately 100°C . and 184°C ., steam and aniline vapour being, in the two cases, passed through all the jackets, J_1 , J_2 , J_3 and K. The results obtained served to determine accurately to within 1 per cent., the dependence of the discharge of air through the orifice upon the density of the air, and were employed in subsequent calculations to determine the respective discharges through the orifice, of hydrogen, coal gas, and carbon dioxide under pressures ranging from 0 to 25 cm. of water. The air-entrainment determinations with these three latter gases were made in a slightly different manner from those in the

* Phil. Mag. *loc. cit.* p. 983.

† Phil. Mag. *loc. cit.* pp. 970-972.

case of air. The gases carbon dioxide and coal gas were stored in a large glass aspirator, and were dried by passage over calcium chloride before being delivered to the discharge tube. The pressure at the orifice fell gradually, and simultaneous readings were taken of the pressure at the orifice and the anemometer reading. The discharge of gas was then calculated from the results for air at the corresponding temperature, using the value of the specific gravity of the dry gas sampled from the aspirator, determined by an effusion method, and also, for comparison, calculated from the analysis of the sampled gas in a Bone and Wheeler gas analysis apparatus. In the case of hydrogen a somewhat similar procedure to this was followed, the gas being delivered from a high pressure cylinder and the pressure at the orifice controlled and maintained constant by means of a double reduction pressure regulator supplied by the British Oxygen Company, Ltd.

In subsequent series of experiments, the various jackets were heated to different temperatures, in order to determine the effect produced upon air entrainment by a variation of the density of the medium into which the jet issued.

Results and Discussion.

The mean diameter of the orifice employed was 0.0884 cm. and the corresponding area 0.00614 sq. cm. It was circular and cylindrical to within 0.4 per cent. of its diameter and was punched in a disk of nickel steel (40 per cent. nickel) of thickness 0.0305 cm. The coefficient of linear expansion was about 6×10^{-6} per °C.

(1) Discharge of Air at Different Temperatures.

Fig. 2 shows how the volume of air discharged (reduced in every case to 0°C. and 760 mm. pressure) depends on the excess pressure at the orifice and the temperature of the gas when all the jackets were heated to the same temperature. Logarithms of the discharge are plotted as ordinates against the logarithms of the corresponding pressures as abscissæ, and the "best fitting" straight line drawn through the observations in each case*. The results are expressed analytically in Table I, where formulæ derived as previously explained are given for the respective volume discharges (reduced to 0°C. and 760 mm.) in terms of the excess pressure, ϵ cm. of water, at the orifice.

* Phil. Mag. *loc. cit.* pp. 974-978.

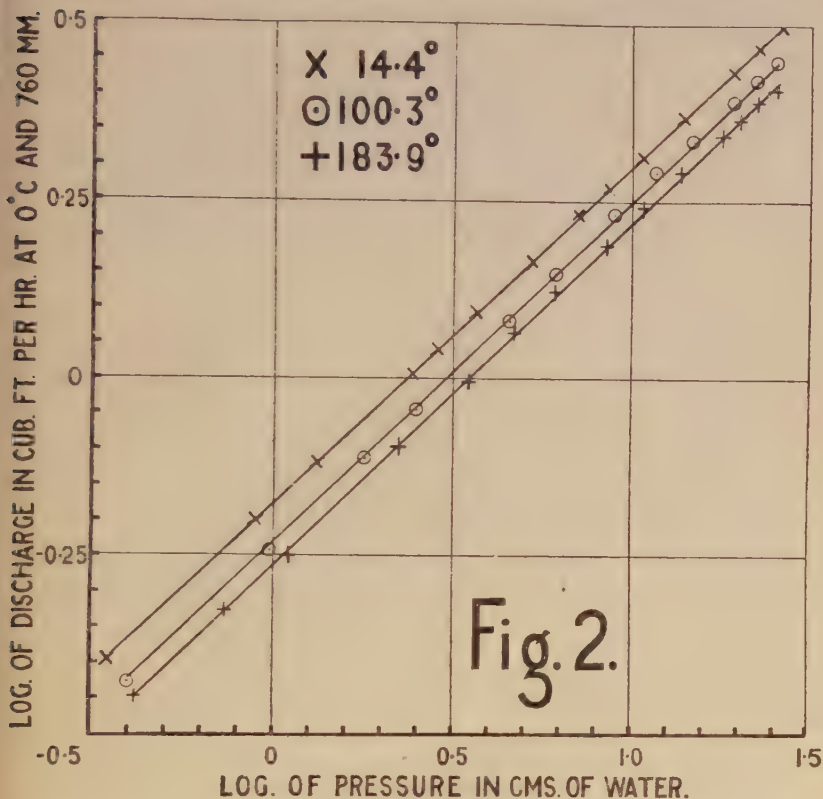


TABLE I.

Temp. of Discharge. ° C.	Empirical formula for discharge in c.c. per sec. reduced to 0°C. and 760 mm. $V = A\epsilon a$.	Corresponding best value of K in $V = S' \left(\frac{2\epsilon/\rho}{\rho_0} \right)^{\frac{1}{2}} \left(1 - \frac{K\epsilon}{\rho} \right)^{\frac{1}{2}}$	S' sq. cm.	Contraction Co- efficient of jet.
14.4	5.250480	3.3	0.00436	0.710
100.3	4.650482	3.0	0.00437	0.711
183.9	4.240486	2.3	0.00440	0.717

We see from the fifth column that the coefficient of contraction of the jet increased by only about 1 per cent. for an increase of temperature of 160°C. To within this

degree of accuracy, the rate of discharge of air (reduced to 0° C. and 760 mm.) through the orifice at a definite excess pressure was proportional to the square root of the density of the air discharged. Within the limits of experimental error the temperatures of the jackets J_1 and J_2 were without influence upon the measured discharge of air. A similar degree of accuracy was obtained between the density of carbon dioxide determined from that of air by an effusion test* and that calculated from analysis of the gas. In the case of coal gas and hydrogen, the difference between experimental and calculated values of the specific gravities relative to air were somewhat greater (1.5 per cent. and 2.5 per cent. respectively). The discharge of these gases at any definite excess pressure has therefore been calculated by means of a formula of the type given in the third column of Table I., employing the appropriate value of the specific gravity of the dry gas determined from the result of an effusion test in which the mean value of the pressure at the orifice was about 12 cm. of water. Thus, *e. g.*, for carbon dioxide (98.63 per cent. CO_2 ; 0.28 per cent. O_2 ; and 1.09 per cent. N_2) at 13°·7 C. and 758.7 mm. pressure, density 0.001967 gm. per c.c. at 0° C. and 760 mm., we use $V = 4.248 \sqrt{\epsilon} (1 - 0.0032 \epsilon)^{\frac{1}{2}}$, the discharge V being measured at N.T.P.

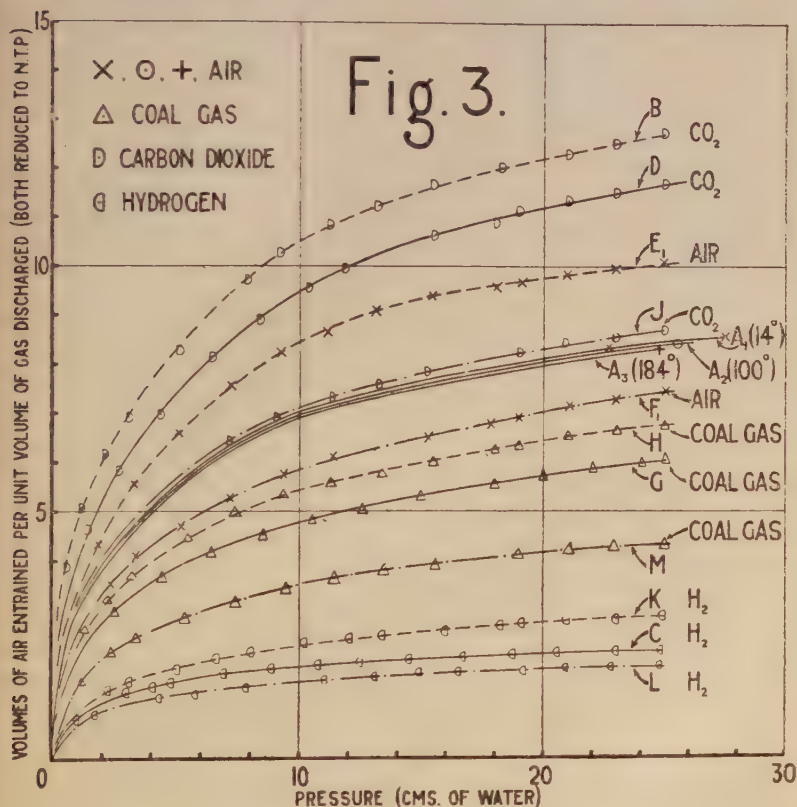
(2) *Air entrainment by the Jet.*

Some of the results obtained for air entrainment by jets of the various gases are shown in fig. 3. Abscissæ represent pressures at the orifice, measured in cm. of water, and the ordinates represent the volumes of air entrained per unit volume of gas issuing in the jet, both volumes being reduced to 0° C. and 760 mm. pressure. We may conveniently describe the ordinates as representing the "aeration" of the jet.

We would first of all direct attention to the three curves A_1 , A_2 , and A_3 , representing the "aeration" of a jet of air at various pressures when discharged at temperatures equal to 14°·1 C., 100°·3 C., and 183°·9 C. respectively, the jet issuing into air at very approximately its own temperature, *i. e.*, so that the density of the air in the jet and into which the jet issues are, at least, very approximately equal. The curves referred to represent the results of experiments in which water, steam, and aniline respectively flowed through *all* the

* See also Edwards, Tech. Paper, No. 94, Bureau of Standards, Washington.

jackets shown in fig. 1. It will be noticed that in each case (and the result is seen to hold generally), the degree of air entrainment effected by the jet increased at first very rapidly and then more slowly as the pressure at the orifice was increased. Similar results were obtained in the case of the experiments detailed in the previous communication.



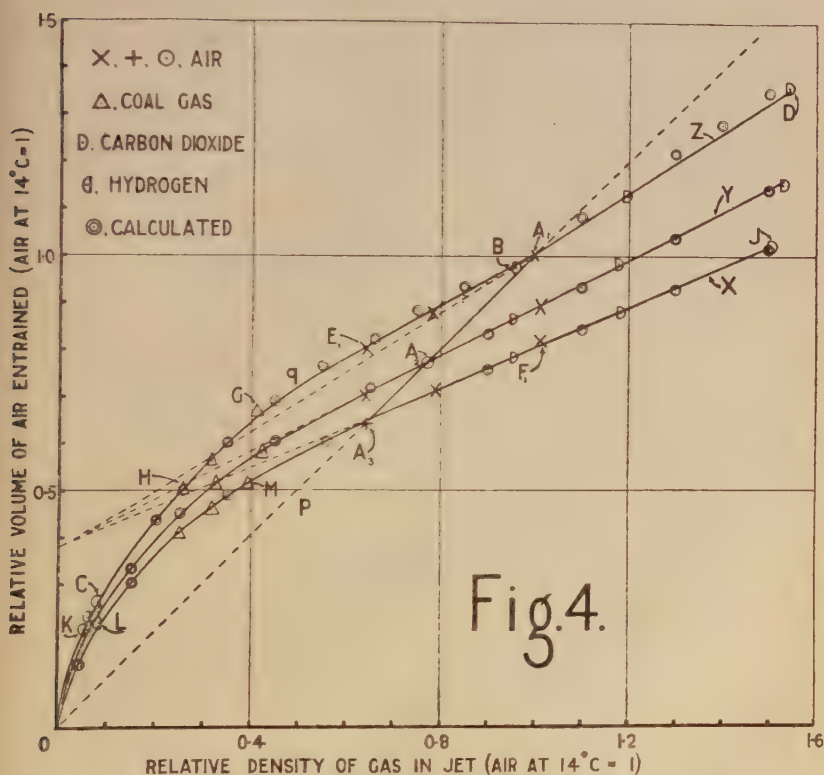
This result is not in agreement with the fundamental result quoted in Technologic Paper No. 193 (1921) of the Bureau of Standards*, wherein it is stated that "over the range of pressure from 2 to 6 inches the ratio of the momentum of the gas stream to the momentum of the air-gas mixture is practically a constant." It is easily shown that on this basis, the degree of air entrainment effected by the jet would be independent of the pressure.

* *Loc. cit.* p. 25.

The curves A_1 , A_2 , and A_3 indicate that when a jet of air issues into air of the same density as that in the jet, the volumes of air entrained at any definite pressure per unit volume of air in the jet (both volumes being reduced to N.T.P.) is practically constant and independent of the density of the air. The curves indicate a decrease of only about 1 per cent. in the percentage aeration of the jet when the temperature of the jet and of the air into which it issued was raised from $14^{\circ}4$ C. to $183^{\circ}9$ C. The decrease is somewhat greater than the estimated experimental error. It will be noticed that this percentage decrease is of the same magnitude as the percentage increase in the contraction coefficient of the jet when the temperature was raised (see Table I.). Owing to this increase in value of the contraction coefficient, the surface area associated with unit volume of the jet (reduced to N.T.P.) will be diminished by approximately 1 per cent. when the temperature of the jet is raised to $183^{\circ}9$ C. Assuming that air entrainment is effected at the surface of the jet, and is proportional to the surface area, it follows that an increase of the contraction coefficient would be accompanied by an equal percentage decrease of aeration of the jet, a deduction which is in accord with the results of the present experiments.

Results obtained when a gas issues under pressure from an orifice into air of less or greater density than the gas in the jet may be illustrated by reference to the curves D and C, which refer to the gases carbon dioxide and hydrogen respectively, the jet of each issuing at $14^{\circ}4$ C. into air at the same temperature. It will be seen that in the case of the heavier gas (carbon dioxide), the aeration of the jet at all pressures is considerably greater than that effected in the case of a jet of air, while in the case of hydrogen, the aeration is similarly considerably smaller. The following procedure was finally adopted for representing in a concise manner the whole of the results obtained. Considering any pair of curves whatsoever, *e. g.*, curves A_1 and B, referring respectively to a jet of air $14^{\circ}4$ C. and a jet of carbon dioxide at $183^{\circ}9$ C. discharged in each case into air at $14^{\circ}4$ C., it was found that the ratio of the respective ordinates of the pair, corresponding to any definite excess pressure at the orifice, was practically a constant throughout the range of pressures employed. This result was found to hold in all cases, and in order to utilize it generally in the case of jets at the same or different temperatures the following procedure was adopted. The respective aerations corresponding to pressures 2, 5, 10, 15,

20, and 25 cm. were read off from the appropriate curve in fig. 3. From these values were calculated the respective degrees of air entrainment effected per unit volume of gas in the jet, reduced to the actual temperature and pressure (barometric) in the jet. The ratios of the respective degrees of air entrainment so calculated to the corresponding degree of aeration effected by a jet of air at $14^{\circ}4$ C., issuing into



air at $14^{\circ}4$ C., taken as a standard, were calculated, and the mean value of the resulting ratio determined. The value so calculated was plotted (see fig. 4) as ordinate against the density of the gas in the jet (under the experimental conditions of temperature and pressure) as abscissa. The procedure will be made clear by consideration of the curves A_1 and B referred to above. (See Table II.)

TABLE II.

Air at 14°·4 C. (Bar. 750·6 mm.) issuing into air at 14°·4 C.		Carbon dioxide at 183°·9 C (Bar. 767 mm.) issuing into air at 14°·4 C.	
Pressure (cms. of water).	Vol. of air entrained per unit vol. of jet (both vols. reduced to N.T.P.).	Vol. of air (reduced to N.T.P.) entrained per unit vol. of jet under experi- mental conditions. (a).	Vol. of air entrained per unit vol. of jet (both vols. reduced to N.T.P.).
			Vol. of air reduced to N.T.P. entrained per unit vol. of jet under experi- mental conditions. (β).
2	4·00	3·76	3·68
5	5·52	5·17	4·94
10	7·00	6·56	6·33
15	7·64	7·16	6·98
20	8·05	7·54	7·37
25	8·41	7·88	7·69
			Mean 0·971

Density of carbon dioxide and air under experimental conditions—0·001164 and 0·001214 grm. per. c.c. respectively.
Ratio of densities (CO_2/air)=0·959.

The value 0·971 for the relative aeration and 0·959 for the relative density of CO_2 are respectively plotted as ordinate and abscissa, and the point B in fig. 4 thus obtained. The

same procedure was followed in all other cases, air at $14^{\circ}\cdot4$ C., issuing into air at $14^{\circ}\cdot4$ C., being throughout made the standard for comparison of density and aeration. It will be noticed that at $183^{\circ}\cdot9$ C. the density of the carbon dioxide in the jet (0.001164) is not very different from that of the air into which it issues (0.001214). The fact that the curves A_1 , A_2 , and A_3 are almost coincident in fig. 3 indicates that results derived from these curves plotted in fig. 4 as described must yield points A_1 , A_2 , and A_3 , lying practically on a straight line passing through the origin. We may say, therefore, that in the case of a jet of air issuing into air of the same density, the volume of air (reduced to N. T. P.) entrained by the jet per unit volume of the jet measured under the experimental conditions of temperature and pressure is strictly proportional to the actual density of the gas under these latter conditions. That this is so for jets of gases other than air issuing into air of the same density as the jet, is seen from the position of the point B corresponding to carbon dioxide issuing at $183^{\circ}\cdot9$ C. into air at $14^{\circ}\cdot4$ C. (respective densities 0.001164 and 0.001214). B lies very nearly on the line $A_1 A_2 A_3$, and only slightly above the corresponding point having the same abscissa on this line. The slight deviation of the position of B from this line is, as will be seen later, in the direction attributable to the slight defect of the density of the carbon dioxide from that of the air into which it issues.

Curve C in fig. 3 refers to a jet of hydrogen at $14^{\circ}\cdot4$ C. issuing into air at the same temperature, and curve D to a jet of carbon dioxide issuing into air under the same condition. The corresponding points in fig. 4 are represented by C and D respectively. It will be seen that in the case of the lighter gas (hydrogen) issuing into a heavier gas (air) the value of the ordinate (point C) in fig. 4 is greater than the value to be anticipated on the assumption that the volume of air entrained per unit volume of the issuing gas (measured under experimental conditions) is proportional to the density of the gas. In the case of a heavier gas (carbon dioxide) issuing into a lighter gas (air) the actual aeration is less than that anticipated on this assumption. Clearly then the degree of aeration of a jet is affected not only by the density of the gas in the jet but also by the density of the medium into which the jet issues. In order to examine this point in detail, experiments were carried out in which the gas flowing through the jet orifice was maintained at various temperatures ($14^{\circ}\cdot4$, 100° C. or $183^{\circ}\cdot9$ C.) while the air entrained was raised to the same or a different temperature

by delivery of cold water ($14^{\circ}\cdot4$ C.), steam, or aniline vapour to the jackets J_1 . Thus in fig. 3 curves A_1 , E_1 , and F_1 refer to air entrainment by a jet of air at $14^{\circ}\cdot4$ C., 184° C., and $14^{\circ}\cdot4$ C., while the air entrained was at temperatures respectively equal to $14^{\circ}\cdot4$ C., $14^{\circ}\cdot4$ C., and 184° C. Similar results for the same temperatures are shown for coal gas, carbon dioxide, and hydrogen by the curves G , H , M ; D , B , J ; and C , K , L respectively. The corresponding points are similarly represented by the appropriate letter in fig. 4, in which various other results in addition to those shown in fig. 3 are plotted. The curves X , Y , and Z thus refer respectively to results obtained when the temperature of the air into which the jet of gas issued was respectively $183^{\circ}\cdot9$ C., 100° C., and $14^{\circ}\cdot4$ C. The result referred to above is seen to be applicable to the whole of the results. Thus considering the curve Y referring to discharge of gas into air at 100° C., it is seen that Y and the straight line $A_1 A_2 A_3$ intersect accurately at the point A_2 , corresponding to conditions of equal density of the issuing gas and of the medium into which the gas issues. For values of the density of the issuing gas greater than that of the air at 100° C. into which it issues, ordinates of the curve Y are less than the corresponding ordinate of the straight line $A_1 A_2 A_3$. Similarly for values of the density of the issuing gas less than that represented by A_2 , ordinates of Y are greater than the corresponding ordinates of $A_1 A_2 A_3$. A similar result is seen to hold when the jet of gas issues into air at $14^{\circ}\cdot4$ C. or $183^{\circ}\cdot9$ C.

These results may be satisfactorily explained as follows :—A jet of gas issuing into air or other gaseous medium is differentiated from a liquid jet issuing into a liquid or gas in that while in the latter case the surface of the jet is well defined, and the properties of the jet determined very largely by surface tension and density considerations*, in the case of the gas jet forces due to surface tension are practically entirely absent. Moreover, considerations of the respective densities of the issuing gas and of the medium into which the gas issues are of increased importance owing to the possibility of a process of diffusion occurring at the surface of the gas jet. In the case of these respective densities being equal, such a process of diffusion will be absent, but an analogous effect is produced by a process of interchange between the jet and the surrounding medium. Consider, however, the case of a gas of density ρ_1 issuing into a gas of different

* See e. g., Smith and Moss, Proc. Roy. Soc. 1917, A. xciii., 373.

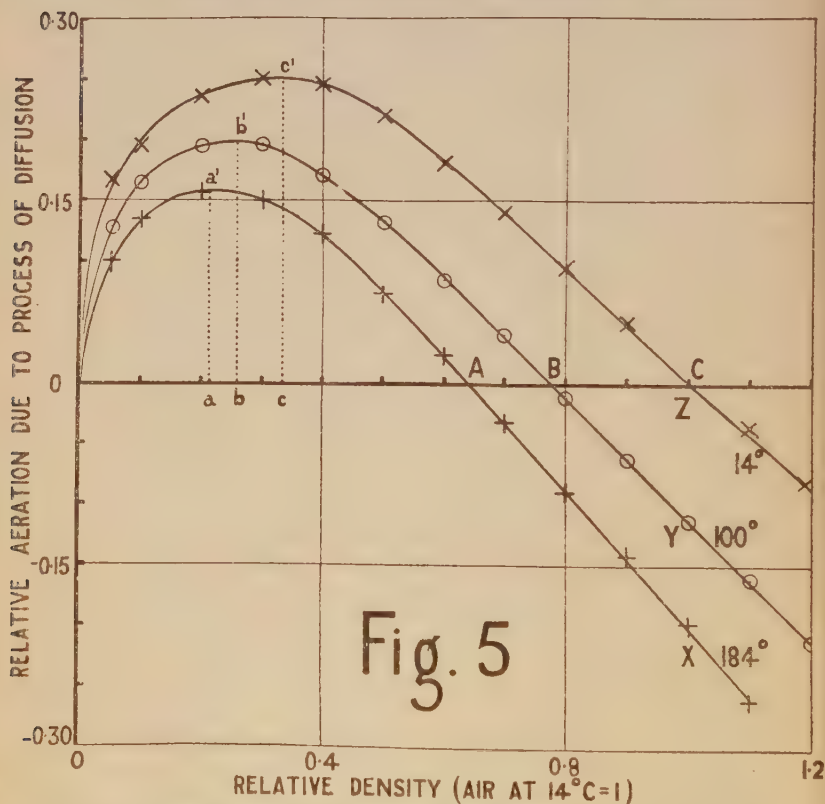
density ρ_2 , at any pressure. Let a fraction, β , of each unit volume of gas discharged diffuse into the surrounding medium. It can easily be seen that the fraction will be, at any definite pressure, at least approximately constant, for, whatever the density of the gas, both the velocity of diffusion of the gas into the surrounding medium and the velocity of discharge of the gas from the orifice at any pressure are inversely proportional to the square root of the density of the gas, and the ratio is therefore a constant. The former velocity is a measure of the tendency of the gas to leave the jet, and the latter is a measure of the tendency of the gas to be retained in the jet. The present assumption of constancy in the value of β will be shown later to be in accord with the experimental results. Consider a volume V of gas discharged in the jet. A volume βV of this gas diffuses into the surrounding gas, and likewise a volume of $\beta V \sqrt{\rho_1/\rho_2}$ of the surrounding gas diffuses into the jet. This diffusion process will continue until a state of equal densities is attained in the jet and the surrounding medium. The volume of gas in the jet becomes $V - \beta V + \beta V \sqrt{\rho_1/\rho_2}$ and the mass is $(V - \beta V)\rho_1 + \beta V \sqrt{\rho_1\rho_2}$. The effective density of the gas is therefore

$$[(V - \beta V)\rho_1 + \beta V \sqrt{\rho_1\rho_2}] / (V - \beta V + \beta V \sqrt{\rho_1/\rho_2}).$$

Expanding as far as the first power of β this expression after a little algebraic reduction gives for the effective density of the jet the value $\rho_1 + \beta(\rho_2 - \rho_1)(\rho_1/\rho_2)^{\frac{1}{2}}$. The result of a process of the nature of diffusion is to increase the effective density of the jet when the jet issues into a medium of high density ($\rho_2 > \rho_1$), and to reduce the effective density when the jet issues into a lighter medium, ($\rho_2 < \rho_1$). The magnitude of such increased or decreased density is, so far as the first power of β is concerned, equal to $\beta(\rho_2 - \rho_1) \times (\rho_1/\rho_2)^{\frac{1}{2}}$. In the equilibrium state the jet issues into a medium of equal density, and as under these conditions the degree of air entrainment is strictly proportional to the density of the gas in the jet (see p. 795), we may say that the increased degree of air entrainment effected due to a process of the nature of diffusion is given by $\alpha\beta(\rho_2 - \rho_1)(\rho_1/\rho_2)^{\frac{1}{2}}$ where α is a constant. The correctness of this result and the limits—if any—within which the formula is valid can be readily tested by means of the experimental data contained in fig. 4. The form of the expression is seen to be in accord with experimental anticipations, for the expression vanishes when $\rho_1 = 0$ and when $\rho_1 = \rho_2$. Moreover, for $\rho_2 \rightarrow 0$, *i. e.*, in the case of a gas issuing into an evacuated vessel, the

expression assumes a large negative value, indicating complete withdrawal of all the gas initially from the jet.

In fig. 5 data derived from fig. 4 as follows have been plotted. Corresponding to any definite abscissa, *e. g.*, 0.5 in fig. 4, the difference pq of the respective ordinates of the curve Z and the straight line $A_1 A_2 A_3$ was determined and plotted in fig. 5 as ordinate against the density of the gas in



the jet (relative to air at 14° C. and 760 mm.), *i. e.*, 0.5 as before. This procedure was followed in the case of each of the curves X, Y, and Z, the respective differences in the values of the ordinates from those corresponding to the straight line $A_1 A_2 A_3$ being determined at intervals of 0.1 in the relative density. The curves so obtained are correspondingly represented by X, Y, and Z in fig. 5. For any individual curve the density of the air into which the jet issues (ρ_2) is a constant. The curves exhibit the relation

between the degree of air entrainment, due to a process of the nature of diffusion occurring at the jet, and the density of the issuing gas, *i. e.*, ordinates are proportional to $\alpha\beta(\rho_2 - \rho_1)(\rho_1/\rho_2)^{1/2}$, conveniently represented by the symbol E , and abscissæ to ρ_1 , while ρ_2 has a constant value appropriate to the respective curves. It has been already pointed out that E vanishes when $\rho_1=0$ and when $\rho_1=\rho_2$. It is of interest

to examine the value of $\frac{dE}{d\rho_1}$. We have $\frac{dE}{d\rho_1} = \frac{\alpha\beta(\rho_2 - 3\rho_1)}{2\sqrt{\rho_1\rho_2}}$,

and when ρ_1 is small, $\frac{dE}{d\rho_1}$ is very large, being equal to

$\frac{1}{2}\sqrt{\frac{\rho_2}{\rho_1}}$. The respective curves therefore are very steep in

the neighbourhood of the origin and cut the axis of abscissæ at right angles. A maximum value of E occurs when

$\rho_1 = \rho_2/3$. Now the values of ρ_2 in the case of the curves in

fig. 5 are proportional to the abscissæ, OA, OB, and OC, which are respectively equal to 0.644, 0.775, and 1.00. It is

seen from the curves that the respective maxima of the curves in fig. 5 correspond very closely with values of the

abscissæ represented by Oa, Ob, and Oc, which are respectively equal to one third of OA, OB, and OC, a result in

agreement with that just deduced from the form of the expression E . Furthermore, the respective maximum values

of E corresponding with $\rho_1 = \rho_2/3$ are given by $2\alpha\beta\rho_2/3\sqrt{3}$, *i. e.*, are proportional to ρ_2 , assuming, as we have done,

that α and β are constants. The experimental values of the maximum ordinates *aa'*, *bb'*, and *cc'* are found, from the

curves in fig. 5, to be in the ratio 0.640 : 0.784 : 1.000 in very close agreement with the corresponding ratio of OA,

OB, and OC, viz. 0.644 : 0.775 : 1.000. The assumption of the constancy of β therefore appears to be justified at least

so far as these values are concerned. Calculating the value of β from these maximum values of E , we find from the

curves X, Y, and Z the respective values 0.646, 0.659, and 0.649 for β . Taking the mean of these we find $E = 0.651\alpha$

$(\rho_2 - \rho_1)\sqrt{\rho_1/\rho_2}$. Hence the relative degree of air entrainment effected by the jet is given by $V = \alpha[\rho_1 + 0.651(\rho_2 - \rho_1)\sqrt{\rho_1/\rho_2}]$.

It will be seen from fig. 4 that for values of the density of the gas into which the jet issues greater than that of the

issuing gas, values of the aeration calculated by means of this formula are in very close agreement with the experimental

values. In cases where the issuing gas is heavier than that into which it issues, the formula affords values of the air

entrainment lower than the experimental values. In this

latter case, the experimental values indicate that a linear relation exists between the degree of air entrainment due to diffusion and the density of the issuing gas. These relations for the cases when a relatively heavier gas issues into air at 14°·4 C., 100° C., and 184° C. respectively are given in Table III. herewith.

TABLE III.

Relation of *E*, the relative air entrainment due to diffusion effected by a jet of gas issuing into a relatively lighter medium.

Temperature of air into which jet issues.	Density relative to air at 14° C. and 760 mm.	Linear relation for $E = -(\gamma\rho_1 + \delta)$.
14°·4 C.	1·000	$-(0\cdot623\rho_1 + 0\cdot38)$
100° C.	0·775	$-(0\cdot508\rho_1 + 0\cdot38)$
184° C.	0·644	$-(0\cdot420\rho_1 + 0\cdot38)$

It is found that the three values of γ given in the third column of the above table are expressed very approximately in terms of the respective values of ρ_2 by the linear relation $\gamma = 0\cdot65\rho_2$ and hence in the case of a jet of gas of density ρ_1 issuing into a lighter gas of density ρ_2 , the degree of air entrainment effected is given by $V = \alpha[\rho_1 - (0\cdot65\rho_1\rho_2 + 0\cdot38)]$. It is interesting to note that the value of the constant 0·65 in this equation is practically the same as that occurring in the relation already deduced for air entrainment effected by a jet of gas issuing into a denser medium (see page 799). This factor and " α " are most probably instrumental constants appropriate to the form of orifice employed, and the dimensions and disposition of the flow system through which the stream of air induced by the jet flows.

Summary.

1. A form of apparatus employing a hot-wire anemometer for the determination of the relative amounts of air entrained by jets of various gases and permitting the densities both of the gas issuing in the jet and that entrained by the jet to be varied within wide limits, is described.

2. It is shown that to within a possible error of 1 per cent. the rate of discharge of air (reduced to 0° C. and 760 mm.) through the orifice employed at a definite excess pressure is

proportional to the square root of the density of the air discharged.

3. When a gas jet issues into air of equal density, the volume of air entrained per unit volume of gas delivered in the jet is strictly proportional to the density of the gas discharged.

4. When the density of the issuing gas is not equal to that of the gas into which it issues, the relation given under (3) no longer applies. In this case the relation between the respective densities of the two gases and the degree of air entrainment effected by the jet is different according as the jet issues into a gas of lower or higher density.

5. In the case of a lighter gas issuing into a heavier gas the volume of air entrained (reduced to N.T.P.) per unit volume of gas issuing in the jet (measured under the experimental conditions of temperature and pressure) is given by $V = \alpha[\rho_1 + \beta(\rho_2 - \rho_1)(\rho_1/\rho_2)^{\frac{1}{2}}]$, where α is the volume of air entrained by a jet of air of standard density, taken as the unit, issuing at the same excess pressure into air of equal density, β is a constant, and ρ_1 and ρ_2 denote respectively the densities of the issuing gas and that of the gas into which the jet issues.

6. The relation given in (5) is deduced on the assumption that a process somewhat analogous to diffusion occurs between the jet and the surrounding medium, and that the result given under (3) is applicable to air entrainment by a jet of gas the density of which tends to become equal to that of the surrounding medium by such process.

7. In agreement with the experimental results, the formula in (5) indicates that air entrainment due to such process of diffusion is a maximum when the density of the issuing gas is one third of that into which the gas issues.

8. In the case of a jet of gas issuing into a lighter medium the corresponding relation for V takes the form $V = \alpha[\rho_1 - (\beta\rho_1\rho_2 + c)]$, where α and β have the same values as in (5) above, and are, it is suggested, instrumental constants, and c is an additional constant.

The work detailed herein was carried out in the Physical Laboratory of the South Metropolitan Gas Company, and the authors desire to express their thanks to Dr. Charles Carpenter and the Directors for their ready provision of all facilities necessary to carry out the work, and for permission to publish the same.

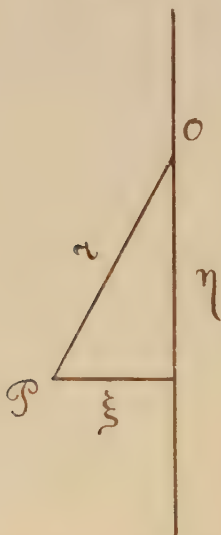
South Metropolitan Gas Company,
709 Old Kent Road, S.E. 15.
July 25, 1923.

LXXXIX. *Diffraction Image of Two Close Luminous Planes.*

By B. E. MOURASHKINSKY, *Optical Laboratory of the Central Chamber of Weights and Measures, Petrograd* *.

THE problem of the resolution of two luminous planes is the same as that of the diffractive conditions of the visibility of a band of finite width on a bright background. The resolving power of an object-glass for two luminous planes depends on the distribution of illumination in the diffraction image of these planes. The illumination at any point in the diffraction image of two planes due to a circular aperture can be expressed in the following manner.

Fig. 1.



The illumination at the point P (fig. 1) in the diffraction image of a point light source is expressed by

$$I_P = \frac{\pi^2 R^4}{\lambda^2 f^2} \cdot \frac{4J_1^2(x)}{x^2}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where

$$x = \frac{2\pi R}{\lambda f} \cdot r, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

r being the distance of the point P from O, the geometrical image of a point source.

* Communicated by the Author.

Integrating (1) with respect to η from $-\infty$ to $+\infty$, we obtain the illumination at the point P due to a narrow line of width $d\xi$. The expression for this integral was obtained by H. Struve * and by Lord Rayleigh †, it is

$$I_l = C_1 \frac{\pi^2 R^4}{\lambda^2 f^2} d\xi \int_{-\infty}^{+\infty} \frac{J_1^2(x)}{x^2} d\eta = C_1 2R \int_z^\infty \frac{J_1^2(x)}{x \sqrt{x^2 - z^2}} dx, \quad (3)$$

where

$$\eta^2 = r^2 - \xi^2;$$

$$\xi = \frac{\lambda f}{2\pi R} z;$$

$$d\eta = \frac{r dr}{\eta} = \left(\frac{\lambda f}{2\pi R} \right)^2 \frac{x dx}{\eta}, \quad (4)$$

ξ being the linear distance of the point P from the geometrical image of a line source.

The integral (3) is calculated by means of the Struve function $H_1(z)$,

$$\begin{aligned} H_1(z) &= \frac{2z^2}{\pi} \int_0^{\frac{\pi}{2}} \sin(z \sin \theta) \cos^2 \theta d\theta \\ &= \frac{2}{\pi} \left[\frac{z^3}{1^2 \cdot 3} - \frac{z^5}{1^2 \cdot 3^2 \cdot 5} + \frac{z^7}{1^2 \cdot 3^2 \cdot 5^2 \cdot 7} - \dots \right]. \quad (5) \end{aligned}$$

The function $H_1(z)$ used here is the same as Gray and Mathews ‡ used in their exposition of Struve's results, it differs from the Struve function $H_1(z)$. The relation between the two functions is

$$\underset{\text{Gr.}}{H_1(z)} = \underset{\text{St.}}{H_1(z)} z.$$

By means of (5) Struve has found that

$$I_l = C_1 2R^2 \frac{2H_1(2z)}{(2z)^3} dz. \quad (6)$$

If we want to express the illumination at the point P in terms of illumination at the geometrical image of a line

* *Mémoires de l'Académie des Sciences de St. Petersburg*, xxx. no. 8 (1882); *Ann. der Phys.* xvii. p. 1008 (1882).

† "Wave Theory," *Encyclopædia Britannica*.

‡ Gray and Mathews, 'Treatise on Bessel's functions,' p. 213 (1922). Our expressions for the constants C_1 and C_2 differ from those of Struve and Gray and Mathews, as they omit the constant factor in the expressions (1) and (9).

source ($z=0$), assumed to be equal to unity, we obtain by means of (5)

$$\left. \frac{2H_1(2z)}{(2z)^3} = \frac{H_1(2z)}{4z^3} \right|_{z=0} = \frac{4\pi}{3} \quad . \quad . \quad . \quad (7)$$

and

$$I_l = C_1 \left. \frac{2R^2 \cdot 2H_1(2z)}{(2z)^3} \right|_{z=0} = C_1 2R^2 \frac{4}{3\pi} dz = 1. \quad . \quad (8)$$

Thus the constant C_1 is determined as

$$C_1 = \frac{3\pi}{8R^2 dz},$$

and (6) takes the form

$$I_l = \frac{3\pi}{4} \cdot \frac{H_1(2z)}{4z^3} = \frac{3\pi}{2} \cdot \frac{H_1(2z)}{(2z)^3} \quad . \quad . \quad (9)$$

If we denote with Lord Rayleigh,

$$L(z) = \frac{\pi}{2} \frac{H_1(2z)}{(2z)^3}, \quad . \quad . \quad . \quad (10)$$

we can write

$$I_l = 3L(z). \quad . \quad . \quad . \quad (11)$$

The function $L(z)$ by means of (5) can be represented by the series

$$L(z) = \frac{1}{1^2 \cdot 3} - \frac{(2z)^2}{1^2 \cdot 3^2 \cdot 5} + \frac{(2z)^4}{1^2 \cdot 3^2 \cdot 5^2 \cdot 7} - \dots \quad (12)$$

If we have to determine the illumination at the point P due to an infinite luminous plane bounded by a straight edge, we can use the following expressions obtained by Struve:

$$I_s = C_2 3 \int_z^\infty L(z) dz, \quad . \quad . \quad . \quad (13)$$

z is equal, as before, to $\frac{2\pi R}{\lambda_f} \cdot r$, where r is the distance of the point P from the geometrical image of the edge. The constant C_2 is determined, if the sought illumination at the point P is expressed in terms of illumination at the same point due to the luminous plane of the same brightness and infinite in all directions. The illumination of the latter is

assumed to be equal to unity, the illumination at the geometrical image of the edge is half of that.

Then

$$I_s = 3 \cdot C_2 \int_z^\infty L(z) dz \Big|_{z=0} = 3 \cdot C_2 \int_0^\infty L(z) dz,$$

and by (5) and (9) it is equal

$$\frac{3\pi^2}{16} C_2 = \frac{1}{2},$$

where from

$$C_2 = \frac{8}{3\pi^2} \dots \dots \dots (14)$$

and

$$I_s = \frac{8}{\pi^2} \int_z^\infty L(z) dz, \dots \dots \dots (15)$$

or

$$\begin{aligned} I_s &= \frac{8}{\pi^2} \int_0^\infty L(z) dz - \frac{8}{\pi^2} \int_0^z L(z) dz \\ &= \frac{1}{2} - \frac{8}{\pi^2} \int_0^z \left[\frac{1}{1^2 \cdot 3} - \frac{(2z)^2}{1^2 \cdot 3^2 \cdot 5} + \frac{(2z)^4}{1^2 \cdot 3^2 \cdot 5^2 \cdot 7} - \dots \right] dz \\ &= \frac{1}{2} - \frac{2}{\pi} \sum_{n=1}^{\infty} (-1)^{n-1} \frac{2n+1}{2n-1} \frac{2^{2n}}{(1 \cdot 3 \cdot 5 \dots 2n+1)^2} z^{2n-1}. \end{aligned} \dots \dots \dots (16)$$

From this

$$I_s(+z) + I_s(-z) = 1, \dots \dots \dots (17)$$

where $I_s(+z)$ refers to the point outside of the geometrical image of a luminous plane and $I_s(-z)$ refers to the point inside of it at the distance z from the image of the edge.

For the expression (15) we have the Struve tables.

If we have a band of width D , where

$$D = \frac{2\pi R}{\lambda f} d, \dots \dots \dots (18)$$

d being a linear width of the geometrical image of a band in the focal plane, the illumination at the point P at the distance z from an image of one (nearer to the point P) edge of a band will be

$$I_b(+z) = \frac{8}{\pi^2} \int_z^{z+D} L(z) dz, \dots \dots \dots (19)$$

$$I_b(-z) = \frac{8}{\pi^2} \int_{-z}^{D-z} L(z) dz, \dots \dots \dots (20)$$

The $I_b(+z)$ refers to the point outside of the image of a band, $I_b(-z)$ to the point inside of it. These integrals can be easily calculated by means of the mentioned Struve tables in the following manner :

$$I_b(+z) = \frac{8}{\pi^2} \int_z^\infty L(z) dz - \frac{8}{\pi^2} \int_{D+z}^\infty L(z) dz, \quad (21)$$

$$I_b(-z) = \frac{8}{\pi^2} \int_{-z}^\infty L(z) dz - \frac{8}{\pi^2} \int_{D-z}^\infty L(z) dz. \quad (22)$$

All the four integrals are to be taken directly from Struve's tables. At the axis of a band $\left(z = -\frac{D}{2}\right)$, we have

$$I_b\left(-\frac{D}{2}\right) = \frac{8}{\pi^2} \int_{-\frac{D}{2}}^\infty L(z) dz - \frac{8}{\pi^2} \int_{+\frac{D}{2}}^\infty L(z) dz,$$

or by (17)

$$I_b\left(-\frac{D}{2}\right) = 1 - 2 \cdot \frac{8}{\pi^2} \int_{\frac{D}{2}}^\infty L(z) dz. \quad (23)$$

At the geometrical image of the edge of a band ($z=0$) we have

$$\begin{aligned} I_b(0) &= \frac{8}{\pi^2} \int_0^\infty L(z) dz - \frac{8}{\pi^2} \int_D^\infty L(z) dz \\ &= \frac{1}{2} - \frac{8}{\pi^2} \int_D^\infty L(z) dz. \end{aligned} \quad (24)$$

Let us consider now the general case, namely, two luminous planes with straight edges of brightness a and c and a band between them of width D and brightness b . The illumination at the point P at the distance $+z$ from the nearer edge *inside* of the geometrical image of a band and at the distance $-z$ *outside* of the image of a band will be

$$\left. \begin{aligned} I(+z) &= a \frac{8}{\pi^2} \int_z^\infty L(z) dz + b \frac{8}{\pi^2} \int_{-z}^{D-z} L(z) dz \\ &\quad + c \frac{8}{\pi^2} \int_{D-z}^\infty L(z) dz, \\ I(-z) &= a \frac{8}{\pi^2} \int_{-z}^\infty L(z) dz + b \frac{8}{\pi^2} \int_z^{D+z} L(z) dz \\ &\quad + c \frac{8}{\pi^2} \int_{D+z}^\infty L(z) dz, \end{aligned} \right\} \quad (25)$$

or using the relation (17)

$$\left. \begin{aligned} I(+z) &= b - (a-b) \frac{8}{\pi^2} \int_z^\infty L(z) dz - (c-b) \frac{8}{\pi^2} \int_{D-z}^\infty L(z) dz, \\ I(-z) &= a - (b-a) \frac{8}{\pi^2} \int_z^\infty L(z) dz + (c-b) \frac{8}{\pi^2} \int_{D+z}^\infty L(z) dz. \end{aligned} \right\} \quad (26)$$

If two planes are of equal brightness ($a=c$) (26) may be written

$$\left. \begin{aligned} I(+z) &= b + (a-b) \left[\frac{8}{\pi^2} \int_{D-z}^\infty L(z) dz + \frac{8}{\pi^2} \int_z^\infty L(z) dz \right], \\ I(-z) &= a + (a-b) \left[\frac{8}{\pi^2} \int_{D+z}^\infty L(z) dz - \frac{8}{\pi^2} \int_z^\infty L(z) dz \right] \end{aligned} \right\} \quad (27)$$

At the axis of a band ($z = +\frac{D}{2}$) we have

$$I\left(+\frac{D}{2}\right) = b + (a-b) 2 \cdot \frac{8}{\pi^2} \int_{\frac{D}{2}}^\infty L(z) dz. \quad (28)$$

At the geometrical image of one edge of a band the illumination will be

$$I(0) = (a+b) \cdot \frac{1}{2} + (a-b) \frac{8}{\pi^2} \int_D^\infty L(z) dz. \quad (29)$$

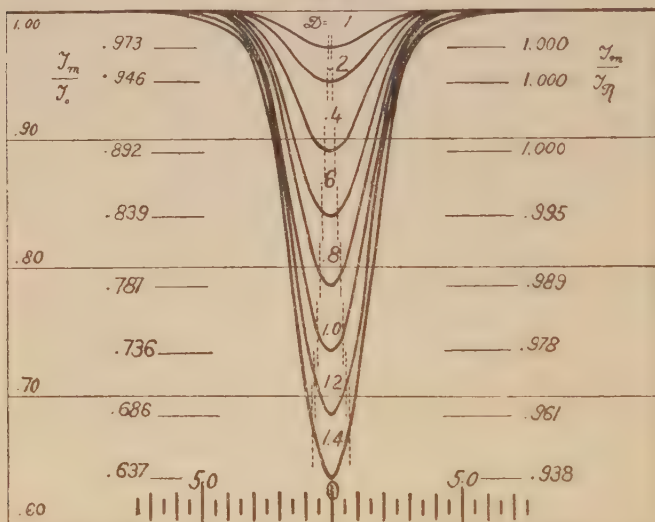
By means of (27), (28), and (29) the distribution of illumination in a focal plane of an object-glass for different values of b and for different values of D may be easily calculated.

Two luminous sources with straight edges (lines, bands, infinite planes with straight edges) have a more simple diffraction pattern in a focal plane of an object-glass than two luminous points or disks, as all the isophotes of the first are always straight lines parallel to the edge. It is sufficient to know the distribution of illumination along one line perpendicular to the edge. We calculated it by means of (27) firstly for the case of $b=0$, i. e., for two luminous planes of equal brightness with a dark band of width D between them for different values of D , from $D=0.1$ to $D=5.0$. The results for some values of D are given in fig. 2.

We shall note five characteristic points of these curves: (1) the point of minimum illumination at the axis of a

central band; (2) two points corresponding to the geometrical images of the edges; (3) two points at which the illumination differs from the general illumination but by a fraction of percentage, say at which it is equal to 0.995. The values of illumination at the axis and that at the image of the edges are given in the second columns of the Tables I. and II.

Fig. 2.



We see that the illumination at the axis for small values of D differs little from the illumination at the edges. For $D=1.0$ and $D=1.4$ the illumination at the axis is about 0.98 and 0.94 of that at the edges respectively, but for greater values of D this ratio decreases very rapidly, so for $D=4.0$ and $D=5.0$ the illumination at the axis is only about 0.36 and 0.28 of that at the edges. These values of illumination at the axis in terms of that at the edges are given in the Table III. and fig. 5. The figures of Tables I., II., III. are correct to 2-3 units of fourth decimal.

The points at which the illumination is nearly equal to general illumination for small values of D are close together, so that the distance of such points on one side of the image for $D=0.1$ and for $D=2.0$ is only about 4.0, i. e., it is approximately equal to the limit of resolution of the eye (for two luminous points) and practically the positions of these points on the curves may be considered as coincident.

The points of the curves on fig. 2 corresponding to the geometrical images of the edges are marked by dotted lines.

TABLE I.

D.	b=	0.	0.1.	0.2.	0.3.	0.4.	0.5.	0.6.	0.7.	0.8.	0.9.
0.19730	.9757	.9784	.9811	.9838	.9865	.9892	.9919	.9946	.9973
0.29460	.9514	.9568	.9622	.9676	.9730	.9784	.9838	.9892	.9946
0.48922	.9030	.9138	.9245	.9353	.9461	.9569	.9677	.9784	.9892
0.68390	.8551	.8712	.8873	.9034	.9195	.9357	.9517	.9678	.9839
0.87868	.8081	.8294	.8508	.8721	.8934	.9147	.9360	.9574	.9788
1.07356	.7620	.7885	.8149	.8414	.8678	.8942	.9207	.9471	.9736
1.26856	.7170	.7485	.7799	.8114	.8428	.8742	.9057	.9371	.9686
1.46374	.6737	.7099	.7462	.7824	.8187	.8550	.8912	.9275	.9634
1.65910	.6319	.6728	.7137	.7546	.7955	.8364	.8773	.9182	.9591
1.85464	.5918	.6371	.6825	.7278	.7732	.8186	.8639	.9093	.9546
2.05042	.5538	.6034	.6529	.7025	.7521	.8017	.8513	.9008	.9504
2.24642	.5178	.5714	.6249	.6785	.7321	.7857	.8393	.8928	.9464
2.44264	.4838	.5411	.5985	.6558	.7132	.7706	.8279	.8853	.9426
2.63912	.4521	.5130	.5738	.6347	.6956	.7565	.8174	.8782	.9391
2.83586	.4227	.4869	.5510	.6152	.6793	.7434	.8076	.8717	.9359
3.03284	.3956	.4627	.5299	.5970	.6642	.7314	.7985	.8657	.9328
3.23008	.3704	.4406	.5106	.5805	.6504	.7203	.7902	.8602	.9301
3.42758	.3481	.4206	.4931	.5655	.6379	.7103	.7827	.8552	.9276
3.62530	.3277	.4024	.4771	.5518	.6265	.7012	.7759	.8506	.9253
3.82326	.3093	.3861	.4628	.5396	.6163	.6930	.7698	.8465	.9233
4.02146	.2914	.3717	.4502	.5288	.6073	.6858	.7644	.8429	.9215
4.21986	.2787	.3589	.4390	.5192	.5993	.6794	.7596	.8397	.9200
4.41846	.2661	.3477	.4292	.5108	.5923	.6738	.7554	.8369	.9185
4.61724	.2552	.3379	.4207	.5034	.5862	.6690	.7517	.8345	.9172
4.81620	.2458	.3296	.4137	.4972	.5810	.6648	.7485	.8324	.9162
5.01530	.2377	.3224	.4071	.4918	.5765	.6612	.7459	.8306	.9153

TABLE II.

Γ .	$b =$	0.	0.1.	0.2.	0.3.	0.4.	0.5.	0.6.	0.7.	0.8.	0.9.
0.19730	.9757	.9784	.9811	.9838	.9865	.9892	.9919	.9946	.9973
0.29461	.9515	.9569	.9623	.9677	.9730	.9784	.9838	.9892	.9946
0.48934	.9041	.9147	.9254	.9360	.9467	.9574	.9680	.9787	.9893
0.68428	.8585	.8742	.8900	.9057	.9214	.9371	.9528	.9686	.9843
0.87955	.8160	.8364	.8568	.8773	.8978	.9182	.9386	.9591	.9796
1.07521	.7769	.8017	.8265	.8513	.8760	.9008	.9256	.9504	.9752
1.27132	.7419	.7706	.7992	.8279	.8566	.8853	.9140	.9426	.9713
1.46793	.7114	.7434	.7755	.8076	.8396	.8717	.9038	.9359	.9679
1.66504	.6854	.7203	.7553	.7902	.8252	.8602	.8951	.9301	.9650
1.86265	.6638	.7012	.7386	.7759	.8132	.8506	.8880	.9253	.9626
2.06073	.6465	.6858	.7251	.7644	.8036	.8429	.8822	.9215	.9607
2.25923	.6361	.6738	.7146	.7554	.7962	.8369	.8777	.9185	.9592
2.45810	.6299	.6648	.7067	.7486	.7905	.8324	.8743	.9162	.9581
2.65728	.6155	.6582	.7010	.7437	.7864	.8291	.8718	.9146	.9573
2.85670	.6103	.6536	.6969	.7402	.7835	.8268	.8701	.9134	.9567
3.05630	.6067	.6504	.6941	.7378	.7815	.8252	.8689	.9126	.9563
3.25602	.6042	.6482	.6921	.7361	.7801	.8241	.8681	.9120	.9560
3.45581	.6023	.6465	.6907	.7349	.7790	.8232	.8674	.9116	.9558
3.65564	.6008	.6451	.6895	.7338	.7782	.8226	.8669	.9113	.9556
3.85547	.5992	.6438	.6883	.7328	.7774	.8219	.8664	.9109	.9555
4.05528	.5975	.6422	.6870	.7317	.7764	.8211	.8658	.9106	.9553
4.25506	.5955	.6405	.6854	.7304	.7753	.8202	.8652	.9101	.9551
4.45484	.5936	.6387	.6839	.7290	.7742	.8194	.8645	.9097	.9548
4.65459	.5913	.6367	.6821	.7275	.7730	.8181	.8638	.9092	.9546
4.85434	.5891	.6347	.6804	.7260	.7717	.8171	.8630	.9084	.9543
5.05410	.5869	.6328	.6787	.7246	.7705	.8161	.8623	.9082	.9541

Fig. 3.

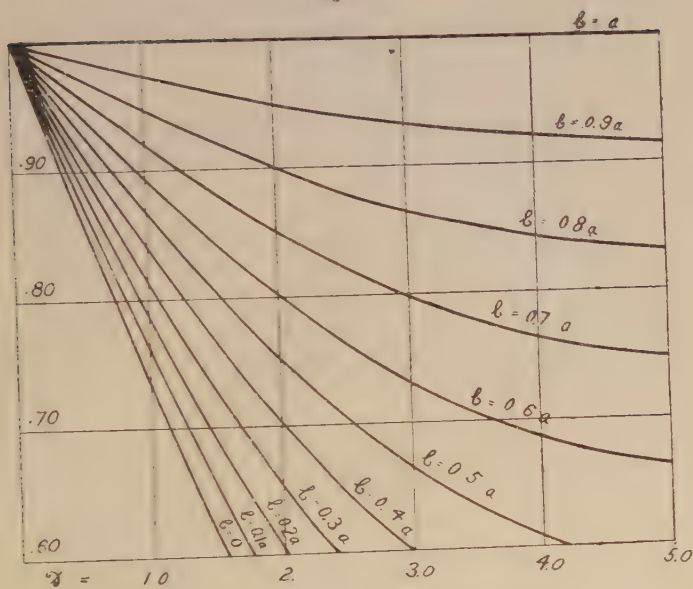


Fig. 4.

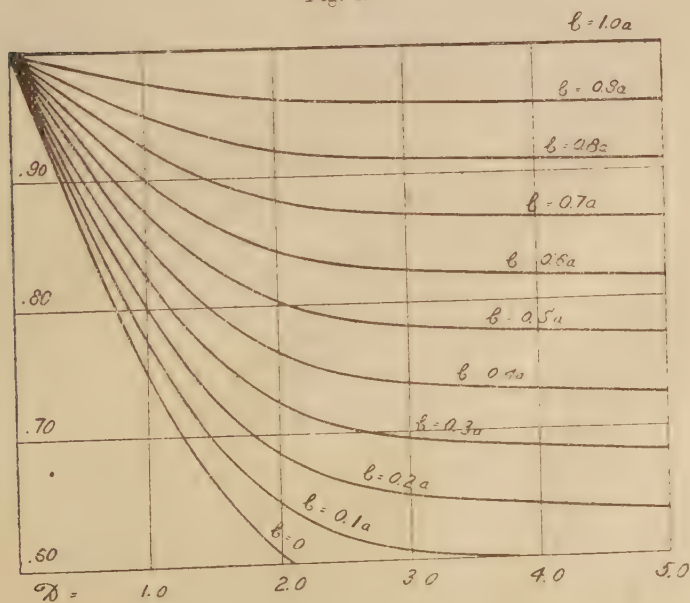
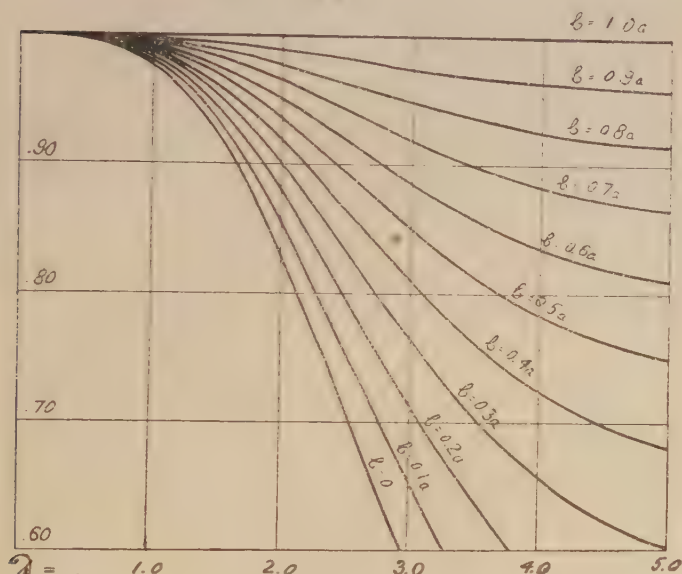


TABLE III.

D.	b = 0.	0.1.	0.2.	0.3.	0.4.	0.5.	0.6.	0.7.	0.8.	0.9.
0.1	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
0.2	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
0.4	.9988	.9990	.9990	.9993	.9994	.9994	.9995	.9997	.9997	1.0000
0.6	.9960	.9966	.9970	.9975	.9979	.9985	.9985	.9988	.9992	.9996
0.8	.9903	.9916	.9930	.9939	.9949	.9962	.9962	.9972	.9982	.9992
1.0	.9808	.9835	.9860	.9884	.9906	.9927	.9927	.9947	.9965	.9984
1.2	.9664	.9713	.9758	.9801	.9839	.9875	.9875	.9909	.9942	.9972
1.4	.9583	.9649	.9692	.9751	.9788	.9808	.9808	.9861	.9910	.9954
1.6	.9470	.9541	.9619	.9688	.9723	.9723	.9723	.9801	.9872	.9939
1.8	.9315	.9419	.9520	.9630	.9708	.9729	.9729	.9827	.9917	.9983
2.0	.9155	.9286	.9404	.9519	.9608	.9650	.9650	.9775	.9893	
2.2	.8987	.9137	.9275	.9398	.9502	.9588	.9588	.9720	.9867	
2.4	.8821	.8987	.9143	.9282	.9409	.9522	.9522	.9663	.9838	
2.6	.8657	.8839	.9015	.9174	.9324	.9465	.9465	.9622	.9810	
2.8	.8495	.8693	.8896	.9081	.9258	.9428	.9428	.9602	.9783	
3.0	.8335	.8559	.8784	.8992	.9190	.9386	.9386	.9586	.9754	
3.2	.8177	.8427	.8677	.8886	.9093	.9297	.9297	.9503	.9679	
3.4	.8021	.8296	.8571	.8795	.9019	.9241	.9241	.9454	.9635	
3.6	.7867	.8170	.8483	.8724	.8969	.9214	.9214	.9434	.9623	
3.8	.7715	.8054	.8396	.8664	.8932	.9200	.9200	.9426	.9619	
4.0	.7564	.7943	.8325	.8624	.8922	.9200	.9200	.9432	.9633	
4.2	.7415	.7833	.8255	.8583	.8922	.9200	.9200	.9432	.9646	
4.4	.7267	.7724	.8196	.8564	.8922	.9200	.9200	.9432	.9652	
4.6	.7121	.7617	.8129	.8524	.8922	.9200	.9200	.9432	.9658	
4.8	.6976	.7512	.8064	.8488	.8922	.9200	.9200	.9432	.9664	
5.0	.6832	.7407	.7999	.8452	.8922	.9200	.9200	.9432	.9670	

In the case of $b > 0$, i. e., when the band has some brightness, the latter is expressed in terms of a —brightness of the planes being assumed to be equal to unity. The values of illumination at the axis and that at the edges are given in the Tables I. and II., and for some values of D and b in figs. 3 and 4.

Fig. 5.



We see that the illuminations at the axis for small values of D do not differ much the one from the other with increasing b , but with increasing D the difference of illumination at the axis for different b increases rapidly. The curves of fig. 3 representing the illumination at the axis for different D and b approach asymptotically the value of b . As b increases the value of D , for which the illumination at the axis differs but very little from b , decreases rapidly; for example, for $D=5.0$ and $b=0.9$ the illumination is about 0.91.

The illuminations at the geometrical images of the edges, as shown in the Table II. and fig. 4, differ more and more with increasing D (b being constant) and with decreasing b (D being constant).

If $b > a$, say $b=1.10, 1.20, 1.30$, etc., the curves in figs. 3

and 4 will be symmetrical with the curves for $b=0.9, 0.8, 0.7$, etc., with respect to the line $b=1.0$.

The diffraction conditions of visibility of a band of width D and brightness b on a background of brightness a seen by means of an object-glass depend on the contrast between the illumination at the axis of a band and that of the background in their diffraction image and on the contrast sensibility of the eye. The latter has been determined in different ways and by several authors, but only for two adjacent fields. As the limit of contrast sensibility of the eye we can admit 2 per cent. for the most favourable conditions of brightness of the fields. For a diffraction image of a band on a bright background the case of adjacent fields cannot be applied. We have no experimental determination of contrast sensibility of the eye for the case when the illumination of field has some minimum with slow or rapid increasing to general illumination.

Michelson* has investigated this case theoretically for an object-glass with a rectangular aperture and found that a dark line on a bright background is still visible when its width is 50 times less than the limit of resolution for two fine lines, the latter being admitted equal to π (Lord Rayleigh criterium). Michelson in his considerations used as limit of contrast sensibility of the eye 2 per cent., but for the distance $=\pi$, the percentage difference of illumination at maximum and at central minimum in a diffraction image of two fine lines is equal to about 20 per cent. (Rayleigh), so even if the conditions of visibility of a band of width D and the conditions of resolution of two fine lines at distance D may be considered identical, the band of width D is visible only 5 times easier than two lines resolved.

If we call critical distance the distance between two planes or the width of a *dark* band between them, for which the percentage difference of illumination at the axis of a band and that at a sufficient distance from it in their diffraction image is equal to zero, the critical distance is equal to zero. (For two luminous points of equal brightness the critical distance will be that for which the percentage difference of illumination at maximum, at or near the geometrical image of one point, and that at central minimum is equal to zero; it is equal to $D=3.0$.)

If we assume as limit of contrast sensibility of the eye 5, 10, 15, 20 per cent. two planes must be at the following distances for different values of b , so as to be resolved by the eye.

* Astrophysical Journal, ii. p. 60 (1895).

TABLE IV.

b .	5.	10.	15.	20.
0	0.17	0.37	0.55	0.73
0.1	0.18	0.41	0.62	0.83
0.2	0.23	0.45	0.72	0.95
0.3	0.26	0.53	0.80	1.08
0.4	0.27	0.61	0.96	1.28
0.5	0.38	0.75	1.14	1.56
0.6	0.47	0.94	1.46	2.04
0.7	0.62	1.30	2.01	2.97
0.8	0.94	2.01	3.60	—
0.9	2.14	—	—	—

These distances expressed as D may be easily converted into angular distances by means of (18). For comparison I give here the corresponding distances for two luminous points of equal brightness on a dark background from my paper "Diffraction Pattern in a case of two very close Point-Light Sources" * :

5.	10.	15.	20.
3.28	3.43	3.56	3.68

If we admit, *rather arbitrarily*, the limit of contrast sensibility of the eye for the case of diffraction image of two planes with a band between them to be 10–15 per cent., we shall have that two planes with a dark band between them ($b=0$) are resolved 9–6 times easier than two points, if generally the conditions of resolution of two planes and two points may be considered identical. For $b>0$ the distances between two planes to be resolved must be greater (see Table IV.). When $a-b$ is less than the assumed limit value of contrast sensibility of the eye, two planes cannot be resolved (see the last line of Table IV.).

A diffraction image of two luminous planes with a dark band or a band of some brightness between them may serve as a convenient object for determining the contrast sensibility of the eye, as we can vary the contrasts within large limits, their calculation is very simple and generally the distribution of illumination in such a diffraction image is clearly definite as all the isophotes are straight lines.

The author is much indebted to Mr. G. Wahrlich for the execution of the drawings.

* Phil. Mag. xlv. p. 29 (1923).

XC. *Note on the Striking Potential necessary to produce a Persistent Arc in Vacuum.* By F. SIMEON, B.Sc., F.Inst.P., Physicist in the Research Laboratories of Adam Hilger, Ltd.*

THE ease with which an arc can be struck in air between two electrodes of carbon or of such a metal as copper and the convenience of such an arc as a light source in spectroscopy, have suggested to those who have experimented in vacuum spectroscopy that an arc *in vacuo* would be convenient and desirable in that region also. When tried, however, it is found that with a number of substances the arc is intermittent when the voltage available for striking is of the order of 100–200 volts. In addition, it is well known that arcs *in vacuo* emit radiations corresponding to the spark lines of the element in question.

In the course of some experiments on the spectrum of carbon in vacuum, its appearance was noted when the applied voltage had several values. For 40 volts or more the arc was as persistent as in air, but the distance between the electrodes could not be made so great, this distance depending upon the voltage and the time the arc had been running (*i. e.*, probably on the temperature of the electrodes). When the striking potential was reduced to 30 volts, the arc would no longer persist, a momentary flash only being produced when the electrodes were slightly separated after being touched together, the appearance being similar to that obtained with two copper electrodes for a striking potential of 220 volts. A marked change in the spectrum of the arc occurred simultaneously with the change in appearance. A striking potential of 40 volts was sufficient to excite the complete spectrum as given by 220 volts, including the lines near 385A, identified by Millikan† as the $L\alpha$ lines of carbon; but with 30 volts the $L\alpha$ and some associated lines were suppressed, still leaving, however, a number of recognized spark lines—*e. g.*, 2297, 2509, and 2512 A. This shows that the lower potential is sufficient to ionize carbon atoms by removal of one of the outer electrons, but insufficient to excite radiation corresponding to the L levels.

To test whether there is a connexion between L radiation and the persistence of the arc *in vacuo*, arcs were formed

* Communicated by Prof. A. W. Porter, D.Sc., F.R.S.

† Millikan, *Astrophys. Journ.* lii. pp. 47–64 (July 1920).

with the elements Cu, Al, Si, and Na. The results are:—

Element.	Observed voltage.		Calculated voltage.
	More than.	Less than.	
Cu	220	—	950
Al	80	100	87
Si	95	105	100
Na	30	40	34

The second column gives the limits within which the voltage corresponding to the beginning of persistence could be decided on. Means were not to hand for obtaining direct current at about 1000 volts, so that in the case of copper the probable value could not be approached, and only a transitory flash could be obtained on touching the electrodes together and separating them. The limits given for aluminium are wider than for the remaining two elements because of the "sticky" nature of the arc, the electrodes appearing to fuse together at the point of contact, so that the effort to separate them often caused the arc to be made longer than could be maintained.

The numbers given in the third column of the table are obtained from the quantum relation

$$Ve = h\nu,$$

the value assigned to ν being that corresponding to the L lines of the element in question. Siegbahn's* value of wave-length 13.309 Å. was used for copper, and Millikan's† value 372 Å. for sodium. The approximate values for aluminium and silicon were obtained by means of Kossel's Combination Principle,

$$L\alpha = K\beta - K\alpha.$$

A check value for aluminium was obtained by taking Millikan's line at 136 Å. as the limit for this metal, the corresponding voltage being 92.

It is interesting to compare these results in one or two instances with corresponding results for an arc in air at ordinary pressures. An immense amount of work has been done on the carbon arc, and various formulæ given connecting the applied voltage and the length of the arc. Fröhlich‡ established the linear relation

$$V = m + nl,$$

in which m and n are constants. Von Lang has determined

* Siegbahn, *Jarhb. d. Rad.* xviii. (3) pp. 240-292 (1921).

† Millikan, *Nat. Acad. Sci. Proc.* (Oct. 1921).

‡ Fröhlich, *Elektrotechnische Zeitschrift*, iv. p. 150 (1883).

the value $m=35$ volts for carbon. More recently Steinmetz* has given the formula

$$V = V_0 + a \frac{(l+b)}{\sqrt{i}},$$

in which i is the current and V_0 , a and b constants. For carbon he gives $V_0=36$ volts. In this case, therefore, there is good agreement with the vacuum value for carbon ($>30 <40$) and with that given by the quantum relation for the limit of the carbon spectrum as determined by Millikan† at 360 A., viz. 35 volts.

In the case of copper the evidence is conflicting. Von Lang has determined m in Fröhlich's formula as 23·86 volts, while Arons‡ has found the potential difference required to produce an arc 1·5 mm. long carrying a current of 4·5 amperes to be 27 volts in air and 30 volts in pure nitrogen. The low value given by v. Lang is probably explained as being a constant found by extrapolation upon plotting results obtained with arcs of various lengths which had been established sufficiently long to have a plentiful supply of electrons of thermionic origin. The value thus obtained would represent the voltage required to maintain an arc of zero length which had already been formed. It seemed best in this case to observe the appearance of the flash produced when two clean copper electrodes were touched together in air. For a potential difference of 10 volts a small spark was produced which did not have the characteristic green colour of the copper arc, which colour did not appear until about 25 volts difference of potential was attained. When the difference had increased to 30 volts, the arc would almost persist, and did persist at 35 volts. Identical observations were made in the case of aluminium, although for this metal Arons gives the values 39 volts for air and 27 for nitrogen.

It is at least clear from these results of v. Lang and Arons that the potential difference required to initiate a persistent arc in air is not determined by the excitation of the L-series corresponding to the electrodes, but is almost, if not quite, a constant quantity. It would therefore seem that in air the nature of the electrodes is not of importance as regards the voltage required to establish an arc, but that this depends chiefly upon the atmosphere in which it is formed.

* Steinmetz, cf. Pidduck's 'Electricity,' p. 361 (Camb. Univ. Press, 1916).

† Millikan, *Astrophys. Journ.* lii. pp. 47-64 (July 1920).

‡ Arons, *Ann. der Phys.* i. p. 700 (1900).

But it does not seem to be necessary in this case to excite the L-series of the gases in the atmosphere, for the highest value given (*i. e.* Arons' value for aluminium in air) is less than the expected value for nitrogen, and still less than that for oxygen. For the latter gas the limit of the L-series is placed at 248 Å. by Kurth* and at 231 Å. by Millikan†, which correspond to voltages of about 50–55. For nitrogen the corresponding value will be intermediate between this and carbon, and will be expected nearer to the former in view of Mohler and Foote's‡ values for the K series.

It is to be noticed that no suggestion is made regarding the carriers of current in a fully-established arc, a full discussion of which has been given recently by Compton§; but if his views receive acceptance, the above considerations may suggest the origin of the positive ions whose presence gives the positive space-charge which enables sufficient electrons to be present to carry the currents observed in practice.

XCI. *The Two-Dimensional Motion of a Lamina in a Resisting Medium under the Action of a Propeller Thrust.*
By S. LISTER, *M.Sc.* ||

THE "phugoids," or "flight curves," of a lamina moving in a resisting medium under no external forces other than its own weight, have been investigated by F. W. Lanchester¶ and S. Brodetsky**. The object of this paper is to extend the investigation by the introduction of a propeller thrust.

Under Lanchester's assumptions the body has a vanishingly small moment of inertia, the velocity has a direction fixed in the body, and there is no loss of energy. The lamina thus maintains the same mean level throughout the motion.

The assumptions made in this paper are, however, those used by Brodetsky, viz., a large moment of inertia, as in the case of a lamina attached to a heavy engine. Small changes in angular velocity can then be neglected and the lamina rotates with uniform angular velocity, ω .

* Kurth, *Phys. Rev.* xviii. pp. 461–476 (1921).

† Millikan, *Nat. Acad. Sci. Proc.* (Oct. 1921).

‡ Mohler & Foote, *Phys. Rev.* xix. pp. 434–435 (1922).

§ Compton, *Phys. Rev.* xxi. (3) pp. 266–291 (March 1923).

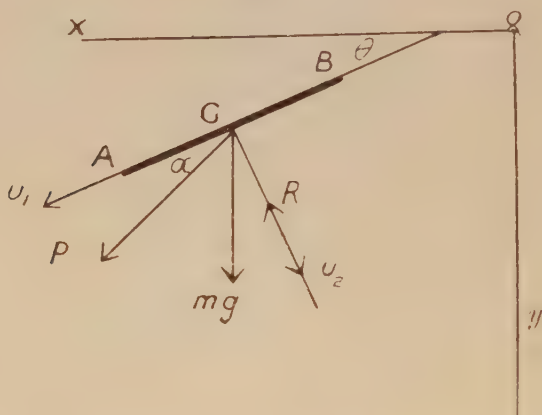
|| Communicated by the Author.

¶ Lanchester, 'Aerodnetics,' Constable, pp. 37–65.

** Brodetsky, *Proc. Roy. Soc. A.* vol. xcv. pp. 516–532 (1919);
'Mechanical Principles of the Aeroplane,' Churchill, pp. 87–93.

The resistance, R , of the medium is assumed to be perpendicular to the lamina, and to pass through G , the centre of gravity.

Fig. 1.



The propeller thrust, P , is inclined at an angle α to the lamina.

The velocities of the lamina along and perpendicular to BA are u_1 and u_2 .

I. *Resistance Proportional to the Velocity:* $R = m\kappa u_2$.

(a) *Constant Propeller Thrust applied along the Lamina:* $P = m\lambda$, $\alpha = 0$, $R = m\kappa u_2$, λ and κ being constants.

The equations of motion are :

$$\left. \begin{aligned} \frac{du_1}{dt} - u_2 \frac{d\theta}{dt} &= g \sin \theta + \lambda, \\ \frac{du_2}{dt} + u_1 \frac{d\theta}{dt} &= g \cos \theta - \kappa u_2, \\ \frac{d^2\theta}{dt^2} &= 0. \end{aligned} \right\} \dots \dots (1)$$

Hence $\dot{\theta} = \omega$; changing the independent variable to θ , and eliminating u_2 , we get

$$\frac{d^2u_1}{d\theta^2} + \frac{\kappa}{\omega} \frac{du_1}{d\theta} + u_1 = \frac{2g}{\omega} \cos \theta + \frac{\kappa g}{\omega^2} \sin \theta + \frac{\kappa \lambda}{\omega^2}.$$

The complementary function has a factor $e^{-\frac{\kappa\theta}{2\omega}}$, and ceases

to be of importance after a time. The particular integral is

$$\left. \begin{aligned} u_1 &= -\frac{g}{\omega} \cos \theta + \frac{2g}{\kappa} \sin \theta + \frac{\kappa \lambda}{\omega^2}, \\ \text{and hence, } u_2 &= \frac{2g}{\kappa} \cos \theta - \frac{\lambda}{\omega}. \end{aligned} \right\} \dots (2)$$

If the time be measured from an instant when $\theta=0$, $\theta=\omega t$. It is now evident from these equations that the motion is periodic, with period $\frac{2\pi}{\omega}$.

The equations of the flight curve, *i. e.*, the path of the centre of gravity, can now be obtained in terms of the parameter θ , since

$$\frac{dx}{dt} = u_1 \cos \theta - u_2 \sin \theta, \quad \text{and} \quad \frac{dy}{dt} = u_1 \sin \theta + u_2 \cos \theta.$$

Substituting, integrating, and choosing the origin so that the terms independent of t vanish, we get

$$\left. \begin{aligned} x &= -\frac{gt}{2\omega} - \frac{g}{4\omega^2} \sin 2\omega t + \frac{\lambda}{\omega^2} \left(\frac{\kappa}{\omega} \sin \omega t - \cos \omega t \right), \\ \text{and} \\ y &= \frac{2gt}{\kappa} + \frac{g}{4\omega^2} \cos 2\omega t - \frac{\lambda}{\omega^2} \left(\frac{\kappa}{\omega} \cos \omega t + \sin \omega t \right). \end{aligned} \right\} \dots (3)$$

By an alteration in the scales in the ratio $1 : \frac{4\omega^2}{g}$, these equations may be written

$$\left. \begin{aligned} x &= -2\theta - \sin 2\theta + 4 \cdot \frac{\lambda}{g} \left(\frac{\kappa}{\omega} \sin \theta - \cos \theta \right), \\ y &= \frac{4\omega}{\kappa} \cdot 2\theta + \cos 2\theta - 4 \cdot \frac{\lambda}{g} \left(\frac{\kappa}{\omega} \cos \theta + \sin \theta \right). \end{aligned} \right\}$$

It will be seen from these equations that the flight curves are trochoidal in form and represent a general fall along the line $y = -\frac{4\omega}{\kappa} \cdot x$, the mean rate of fall being $\frac{2g}{\kappa}$ for all values of λ , including the case of no propeller thrust, ($\lambda=0$).

When $\lambda=0$, the flight curves can, by turning the axes and changing the origin and parameter, be put in the form

$$\left. \begin{aligned} x &= \phi \sec \beta + \sin \phi, \\ y &= \sec \beta - \cos \phi, \end{aligned} \right\}$$

where $\tan \beta = \frac{4\omega}{\kappa}$, and $\phi = 2\theta + \beta$.

The flight curves for no propeller thrust are therefore pure trochoids, without loops or cusps*. The propeller thrust, however, introduces both loops and cusps into the flight curves.

The lamina cannot reproduce its initial motion for any value of the propeller thrust, and hence it can never describe a closed path. There is, in fact, a loss of energy equal in amount to $\int (\kappa u_2^2 - \lambda u_1) dt$ per unit mass, and if the integration be taken over a period, we get $\frac{4\pi g^2}{\kappa \omega}$ for all values of λ . It will be noticed also that, for a given value of ω , the greater the value of κ , the more nearly does the mean path approximate to the horizontal, and the smaller is the loss of energy. Also, the mean rate of fall is just twice as great as if the lamina were to fall as a parachute, and is independent of the rotation†.

Cusps. The cusps are of interest, representing, as they do, the extreme case of "stalling," or loss of flying speed. They occur when the resultant velocity becomes zero and changes its direction through 180° , i.e. when the u_1 , u_2 curves pass through the origin. Hence, for cusps, we have

$$\text{and} \quad \left. \begin{aligned} -\frac{g}{\omega} \cos \theta + \frac{2g}{\kappa} \sin \theta + \frac{\kappa \lambda}{\omega^2} &= 0, \\ \frac{2g}{\kappa} \cos \theta - \frac{\lambda}{\omega} &= 0, \end{aligned} \right\}$$

whence

$$\text{and} \quad \left. \begin{aligned} \tan \theta &= -\frac{\kappa}{2\omega}, \\ \frac{\lambda}{g} &= \frac{2\omega}{\kappa} \cos \theta = \frac{4\omega^2}{\kappa^2} \left(1 + \frac{4\omega^2}{\kappa^2}\right)^{-1/2} \end{aligned} \right\} \quad \dots \quad (4)$$

Loops. For greater values of $\frac{\lambda}{g}$, the cusps develop into loops, and the characteristic features of looping present themselves, viz., the dive to gain speed, the summit of the loop being reached in an upside-down position, and the dive again to regain normal flying speed.

* Edwards, 'Differential Calculus,' p. 343.

† Brodetsky, *loc. cit.*

(b) *Propeller Thrust Inclined at an Angle α to the Lamina.*

The equations of motion are :—

$$\left. \begin{aligned} \frac{du_1}{dt} - u_2 \frac{d\theta}{dt} &= g \sin \theta + \lambda \cos \alpha, \\ \frac{du_2}{dt} + u_1 \frac{d\theta}{dt} &= g \cos \theta - \kappa u_2 + \lambda \sin \alpha, \\ \frac{d^2\theta}{dt^2} &= 0. \end{aligned} \right\} \quad . \quad . \quad (5)$$

Proceeding as in I(a), we get

$$\left. \begin{aligned} x &= -\frac{gt}{2\omega} - \frac{g}{4\omega^2} \sin 2\omega t + \frac{\lambda}{\omega^2} \left(\frac{\kappa}{\omega} \cos \alpha + \sin \alpha \right) \sin \omega t \\ &\quad - \frac{\lambda}{\omega^2} \cos \alpha \cos \omega t, \\ y &= \frac{2gt}{\kappa} + \frac{g}{4\omega^2} \cos 2\omega t - \frac{\lambda}{\omega^2} \left(\frac{\kappa}{\omega} \cos \alpha + \sin \alpha \right) \cos \omega t \\ &\quad - \frac{\lambda}{\omega^2} \cos \alpha \sin \omega t. \end{aligned} \right\}$$

Comparing these with equations (3), and writing $\lambda', \kappa', \omega', g'$, for the values which must be given to $\lambda, \kappa, \omega, g$ in the previous case to obtain the above equations, we have the following substitutions :—

$$\omega' = \omega, \quad g' = g, \quad \lambda' = \lambda \cos \alpha, \quad \kappa' = \kappa + \omega \tan \alpha.$$

The case when $\alpha \neq 0$ is thus reduced to a simple application of that when $\alpha = 0$.

(c) Other cases have been worked out in which attempts were made to allow for the decreasing efficiency of the propeller at higher speeds, *e.g.*, the propeller thrust was assumed to diminish exponentially as the speed of the lamina increased. The manipulation became rather heavy and it is omitted here; the flight curves obtained showed the same characteristic features as those obtained in the preceding cases.

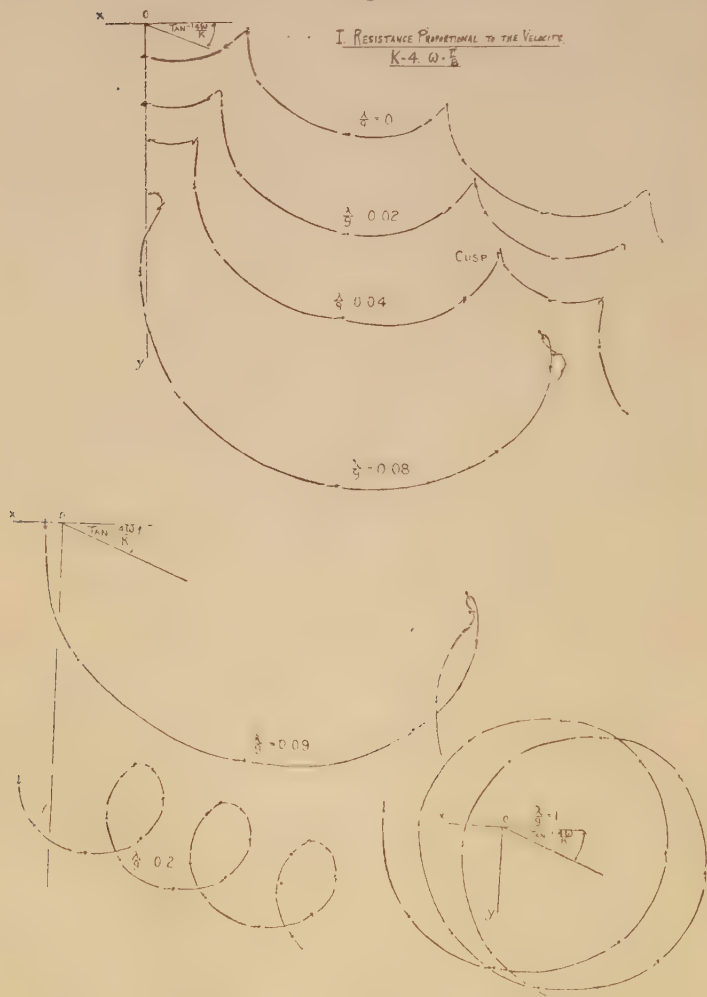
The Flight Curves.

For the most part these were drawn by direct computation from the equations, but in more complicated cases they were obtained by plotting u_1 against u_2 and marking the time intervals on the velocity curves thus obtained. The resultant velocity was easily obtained from the u_1, u_2 curves

from instant to instant, and thence the flight curves were drawn.

In the diagrams shown, the same values of κ and ω are

Fig. 2.



used, so that the mean line of descent is the same for all the flight curves. They aim at showing how the curves change as the propeller thrust is increased.

For zero propeller thrust, the curves are pure trochoids without loops or cusps. For small values of the propeller

thrust, the flight curves have two unequal undulations per period. As the propeller thrust is increased, the smaller undulation decreases in size and the transition crest becomes sharper and sharper, until, finally, it becomes a cusp. On further increasing the propeller thrust, the smaller undulation develops a loop, the loop growing in size until, for values of $\frac{\lambda}{g}$ approaching unity (a very extreme case in practice), the flight curves assume the appearance of a "travelling circle."

II. Resistance Proportional to the Square of the Velocity.

Let the resultant velocity, V , make an angle, γ , with the lamina. Neglecting, for the present, all external forces except the resistance of the medium, and assuming $R = AV^2 \sin \gamma$, where A is a constant, we get as the equations of motion:—

$$\left. \begin{aligned} \frac{du_1}{dt} - u_2 \frac{d\theta}{dt} &= 0, \\ \frac{du_2}{dt} + u_1 \frac{d\theta}{dt} &= -AV^2 \sin \gamma, \\ \frac{d^2\theta}{dt^2} &= 0. \end{aligned} \right\} \dots \dots (6)$$

These reduce to

$$\left. \begin{aligned} \frac{du_1}{dt} &= \omega u_2, \\ \frac{du_2}{dt} + \omega u_1 + Au_2 V &= 0, \\ \dot{\theta} &= \omega; \end{aligned} \right\}$$

and again to

$$\frac{dV}{du_1} = -ku_2, \text{ where } k = \frac{A}{\omega}.$$

This equation does not appear to be integrable in exact terms, and Brodetsky's graphical method of solution is adopted *. k only affects the scale of the curves, and, if the

* Mathematical Gazette, vols. ix. & x., nos. 142, 144-6; and Piaggio, 'Differential Equations,' pp. 5-9.

u_1, u_2 curves be drawn from the equation

$$\frac{dV}{du_1} = -u_2 \dots \dots \dots (7)$$

the radius vector must be multiplied by $1/k$ to obtain the correct value of V^* .

Also, following a suggestion by Prof. L. J. Rogers, the orthogonal trajectories of (7) are easily found.

Since $V^2 = u_1^2 + u_2^2$, we have for the orthogonal trajectories

$$\frac{du_1}{du_2} = \frac{u_1}{u_2} + V.$$

Putting $u_1 = z \cdot u_2$, we get

$$\frac{dz}{du_2} = (1 + z^2)^{1/2},$$

whence

$$u_1 = u_2 \sinh(u_2 + B),$$

B being an arbitrary constant.

Remembering the change of sign on passing through the lamina, the orthogonal trajectories can be plotted, and the solution of (6) obtained in graphical form.

The corrections for the propeller thrust and the weight were then applied and the final u_1, u_2 curves were obtained for $\frac{1}{4}$ -second time intervals. Some of the flight curves are given, but the graphical solution of (7) and the velocity curves are omitted.

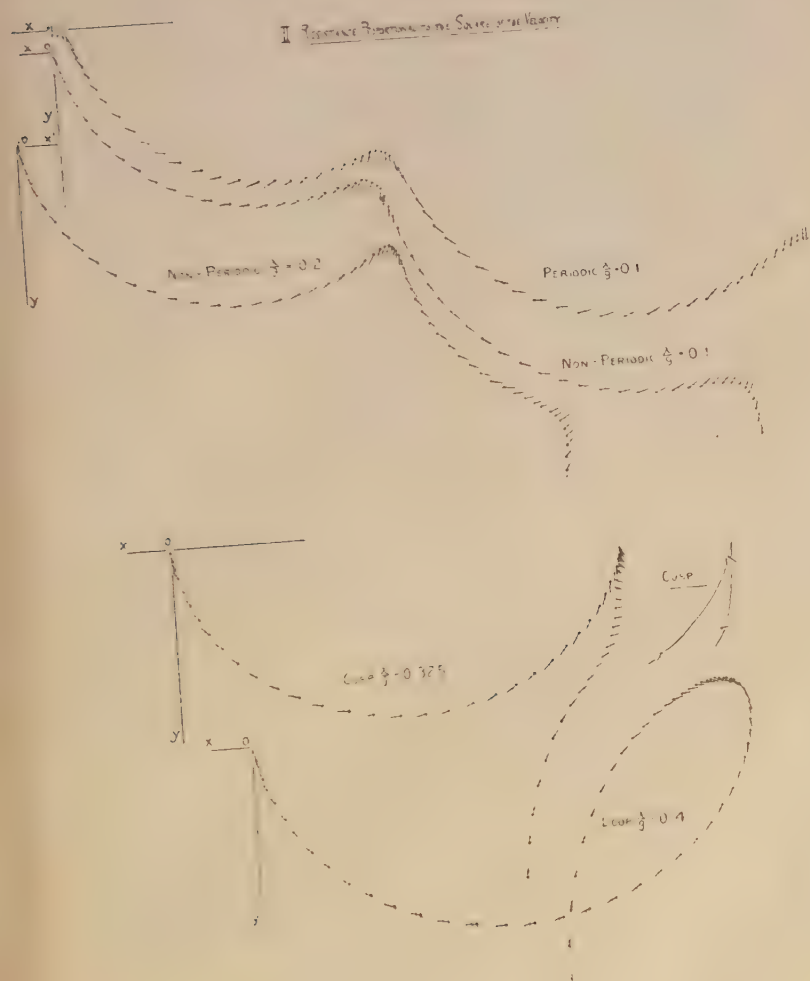
Flight Curves.

It will be noticed that the curves are not in general periodic. To obtain periodic curves it is necessary to obtain u_1, u_2 curves which form a closed path. Cusps are obtained by finding u_1, u_2 curves which pass through the origin. The velocity curves for periodic motion and cusps are obtained by a process of trial and error. Attempts to find a periodic curve with a cusp proved unsuccessful.

It will be seen from the diagrams that the general features, except that of periodicity, are much the same as in the case of the resistance varying as the first power of the velocity, the increase in the propeller force producing the same series of changes as before.

* This analysis is taken from Brodetsky's paper, already referred to above.

Fig. 3.



In conclusion, I desire to express my indebtedness to Dr. S. Brodetsky for suggesting this work, and for his very valuable advice and criticism throughout the investigation.

XCI. *Ionizing Potentials of Helium and some Multiatomic Gases.* By C. A. MACKAY, M.A., 1851 Exhibition Fellow, Princeton University*.

THE study of radiating and ionizing potentials of metallic vapours and monatomic gases has been of great importance in developing the theory of line spectra and atomic structure. In the case of multiatomic gases, the conditions are more complicated, and relatively little progress has been made either in the direction of obtaining comprehensive and reliable experimental data or of relating these data to spectroscopic, chemical, or other properties of the molecules and their constituent atoms. Reviews of the experimental and theoretical aspects of these problems are given by Hughes† and by Foote and Mohler‡.

Born§ and Fajans|| have calculated the ionizing potentials of HCl, HBr, and HI. These have been measured by Knipping,¶ who gives values close to those predicted. Foote and Mohler** also calculated the ionizing potentials to be expected for the case of certain compound gases in which the process of ionization may reasonably be assumed to take the form of splitting up the molecule into positively and negatively charged atoms for which there are sufficient thermochemical data to predict the ionizing potentials. Beyond the metallic vapours—hydrogen, helium, and a few compounds—no ionizing potentials have been calculated, but some correlations have been suggested by Smyth†† and Foote and Mohler‡‡ between the radiating potentials they found and the lines in the spectrum of nitrogen.

In view of this situation, it was considered of importance to investigate as large a number of related multiatomic gases as possible, to serve as a basis of further theoretical developments. The present paper presents the results thus far obtained in an investigation which is to be extended to other gases.

The method employed was suggested by Hughes and

* Communicated by Professor K. T. Compton.

† Bull. Nat. Research Council, vol. ii. pt. 2, No. 10.

‡ 'Origin of Spectra.'

§ *V. d. D. P. G.* vol. xxi. p. 13 (1917).

|| *V. d. D. P. G.* vol. xxi. p. 714 (1919).

¶ *Zeit. f. Phys.* vol. vii. p. 328 (1921); also Franck, *Zeit. f. Phys.* vol. xi. p. 160 (1922).

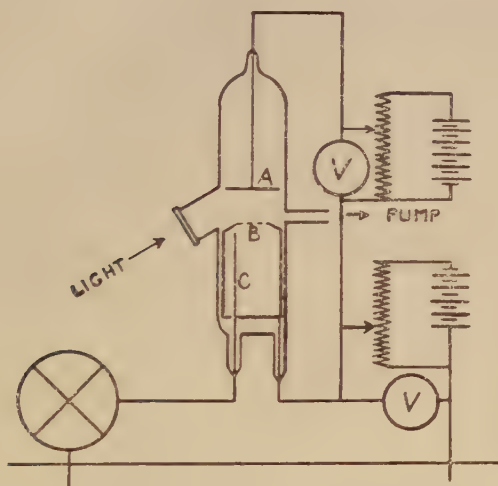
** Journ. Wash. Acad. Sci. vol. x. p. 435 (1920).

†† Phys. Rev. vol. xiv. p. 409 (1919).

‡‡ J. O. S. A. vol. iv. p. 49 (1920).

Dixon *, though it was not the one they finally adopted in their work. A nickel target (A, fig. 1) illuminated by ultraviolet light from a quartz-mercury arc lamp provided a source of electrons. This arrangement had two advantages over a hot filament; it did not decompose the compound gases, and it was not attacked by gases such as oxygen and water vapour. The electrons were accelerated towards the platinum gauze B by means of a variable electric field. Between B and the electrode C a constant difference of potential was maintained in such a direction that positive ions would be attracted to C. In order that a minimum

Fig. 1.



amount of any radiation, emitted by the molecules on electron impact, should fall on C, it was made of a fine platinum wire with extremely small area. As a consequence, the amount of photo-electric effect produced in C was negligible, and thus the apparatus was rendered insensitive to radiation effects. On the other hand, the wire was effective as a collector of ions. The rate at which C became charged was measured by a Compton electrometer with a sensitivity of approximately 2000 mm. deflexion per volt.

The electrons emitted from the surface of the nickel target had kinetic energy varying from zero to that corresponding to about two volts. The distribution of the velocities of the electrons depended on the character of the light from the

* *Phys. Rev.* vol. x. p. 495 (1917).

are lamp, though even if it had been strictly monochromatic, the velocities would not have been uniform. Ionization began as soon as the fastest electrons had kinetic energy equivalent to the ionizing potential, and this energy was the sum of the initial energy of the electrons at the surface of the target together with the energy resulting from the electric field between A and B. Some means had to be found to take into consideration the former energy so that the applied difference of potential plus a correction would give the actual energy of the electrons producing ionization. Several methods which have been used in other work are discussed by Smyth*. They are usually based on some theoretical or experimental curve which shows the velocity distribution of the electrons after they have been accelerated by the applied electric field. In a later paper Brandt† gives a more direct method, which is satisfactory provided the ionizing potential of one substance, which is used as a standard, is accurately known by some independent means. The principal series of the mercury spectrum has a convergence limit corresponding to an ionizing potential of $10\cdot392\frac{1}{2}$: so that mercury was chosen as the standard. If helium is mixed with mercury vapour and the ionizing potentials of both substances are measured, then the difference between the potentials will be the same for any distribution of velocities of electrons used in actual measurements. Neither will corrections due to contact difference of potential between the nickel and platinum electrodes need to be applied, nor will surface effects such as found by Brandt and assumed to be produced by layers of polarized molecules of the gas be a disturbing factor. Let us suppose that the observed values for mercury and helium are $10\cdot2$ and $24\cdot3$ volts. The correction for mercury is evidently $\cdot2$ volt (if $10\cdot4$ is taken as the correct value), and accordingly to keep the difference between the ionizing potentials the same, $\cdot2$ volt must be added to the helium value, making the corrected result $24\cdot5$ volts. Helium was chosen because its high radiating and ionizing potentials would prevent confusion with the critical potentials of any other gases, and its chemical inertness would prevent combination with other gases to be mixed with it. Brandt found that nitrogen, having a lower radiating potential than helium, was unsatisfactory. Having thus obtained the corrected value for helium, it was mixed with another gas and the difference in the ionizing potentials

* Phys. Rev. vol. v. p. 14 (1919).

† *Zeit. f. Phys.* vol. viii. p. 32 (Dec. 1921).

‡ Foote and Mohler, 'Origin of Spectra,' p. 64.

was measured. The difference was subtracted from the corrected value of the ionizing potential of helium, and the result was taken as the corrected value of the ionizing potential of the gas. The corrections varied from $\cdot 1$ to $\cdot 5$ volt in different gases.

To insure that adsorbed gases from the glass were removed, the whole apparatus was exhausted by means of a Langmuir diffusion pump until a McLeod gauge showed no trace of pressure. It was then allowed to stand for 24 hours and re-exhausted. After another equal interval, the experimental tube was "washed out" several times with the gas that was being measured. Either phosphorus-pentoxide or soda-lime tubes were used for drying, and mercury vapour was removed by two traps surrounded by liquid air or carbon-dioxide snow mixed with alcohol. It was found that traces of impurities could be easily detected by a comparison of the curves obtained when they were present with the curves of the pure gas. The most convenient pressures were determined by a few preliminary trials. They varied with different gases, but were all within the limits $\cdot 001$ mm. and $\cdot 05$ mm. of mercury.

Since the helium was used repeatedly, an apparatus was set up to recover and repurify it after every run. This consisted of a Geissler-Toepler pump connected with a small drying-tube and a charcoal trap, so arranged that the helium could be pumped out of the experimental tube and then forced through the trap, which was immersed in liquid air. The gas was stored in the drying-tube. The curves plotted from data for helium showed that the impurities were completely removed by repeated pumping through the charcoal.

The other gases were made by the usual chemical procedure from pure reagents. In the work with water vapour it was found that a convenient vapour-pressure could be obtained if potassium hydroxide was allowed to come to equilibrium with its vapour-pressure at room temperature. Since hydrogen iodide attacks mercury, so that it could not be pumped through the Langmuir pump, the gas was admitted at a pressure rather higher than desired, and the excess was taken up by a tube of fused potassium hydroxide.

Readings were not taken until thirty minutes after the target had been illumined to permit the emission of electrons to become nearly constant. The retarding field between B and C which gave the most satisfactory results was between $6\cdot 0$ and $8\cdot 0$ volts. The accelerating field from A to B was varied by steps of $\cdot 1$ or $\cdot 2$ volt over a range from 0 to 50 volts, with an accuracy of the voltage readings

better than .05 volt. The electrometer deflexions were timed by a stop-watch graduated to .1 second with a probable error less than .05 second. A series of wire screens in front of the lamp were arranged to regulate the intensity of the ultra-violet light so that no reading of less than

Fig. 2.

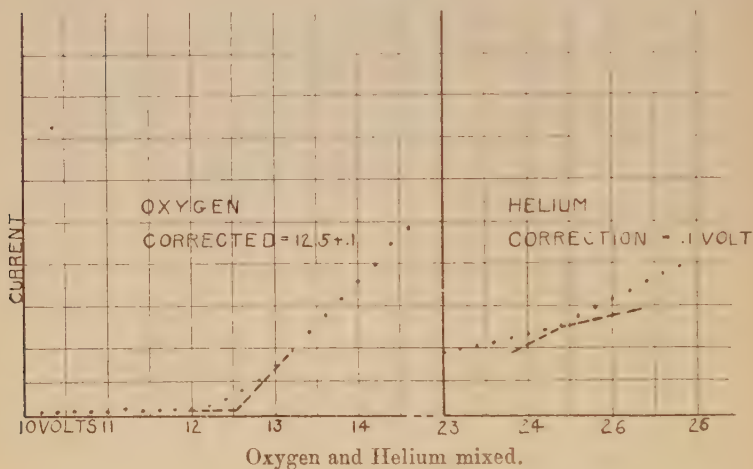
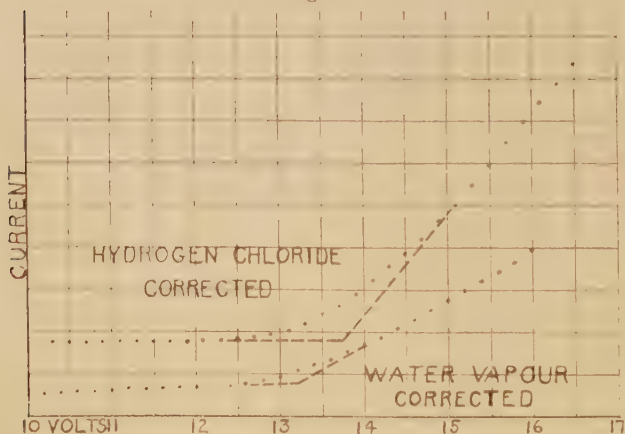


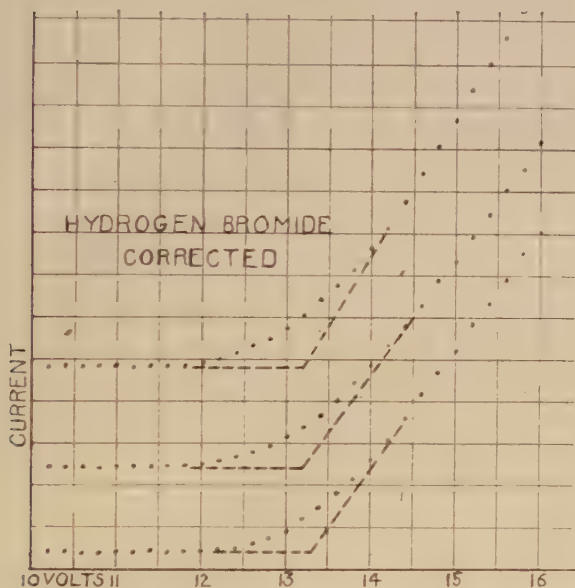
Fig. 3.



10 seconds for 20 cm. deflexion was necessary. The results were plotted, using the accelerating potentials as abscissae, and the reciprocal of the rate of electrometer deflexion, which is proportional to the current reaching the negative electrode, as ordinates.

Typical curves are shown in figs. 2-4. They all had discontinuities, which meant that when the electrons acquired a certain kinetic energy, positive ions were produced and attracted to the negative electrode, which caused the rate of charging of the electrometer to increase suddenly. Since all the electrons did not have the same energy, the break in the curves was never sharp. The fastest electrons, which

Fig. 4.



produced the first ions, were relatively few in number, so that at first the change of slope increased slowly; but as more and more electrons became capable of producing ionization, the rate of change of slope greatly increased. This made it difficult to determine the exact point at which ionization began. If, however, tangents are drawn to the curve below and above a critical point, where the curve is practically a straight line, their intersection is quite definitely located by means of at least 6 or 8 points which determine the position of each tangent. From the method of correction adopted, any characteristic point, connected with the discontinuity in a curve which could be accurately fixed, was a satisfactory point. All that was needed was the difference between the breaks in the curve for helium and the gas in question.

Though the accelerating potential was increased up to 50 volts, in no case was more than one ionizing potential observed. If an electron produced ions by a second collision with a molecule, or if the molecule possessed two ionizing potentials, a second discontinuity might have been expected. Unless such an effect were very strong, it would not have produced a detectable bend in the curves, since the current due to the first ionization was already very large. All that can be stated from the present data is that any second ionization was too weak to be detected in the region up to 50 volts.

The results for the individual gases are as follows:—Mercury (chosen as a standard) 10.4 volts; helium 24.4, 24.4, 24.5, 24.5, 24.6, mean 24.5 volts; nitrogen 16.2, 16.3, 16.3, 16.3, mean 16.3 volts; hydrogen 15.6, 15.7, 15.9, 15.9, mean 15.8 volts; oxygen 12.4, 12.4, 12.5, 12.5, 12.6, 12.7, 12.7, mean 12.5 volts; hydrogen chloride 13.8, 13.8, 13.8, 13.9, mean 13.8 volts; hydrogen bromide 13.0, 13.2, 13.2, 13.2, 13.3, mean 13.2 volts; hydrogen iodide 12.6, 12.8, 12.8, 12.8, 12.9, mean 12.8 volts; ammonia 11.1, 11.1, 11.1, 11.2, mean 11.1 volts; water vapour 13.0, 13.2, 13.3, 13.4 volts, mean 13.2 volts.

In the Table (p. 835), these mean values are compared with the results of other measurements, together with calculated values of the ionizing potential when available.

The value for helium given by the present investigation agrees with the convergence limit of Lyman's spectroscopic series*. It may be pointed out that with the present method it is unnecessary to assume Bohr's principle of selection, as has always been done heretofore, in order to correct the experimental results obtained for helium. The value for oxygen is considerably lower than that given by Foote and Mohler, but agrees with a value indicated on curves published by Hughes and Dixon but not reported by them†. There is good agreement between the calculated values for the halogen acids and the experimental results.

Throughout this investigation, Professor K. T. Compton has given many valuable suggestions and helpful criticisms, for which the writer wishes to express his appreciation.

* Science, vol. lvi, p. 17 (1922).

† *Loc. cit.*

TABLE.

Gas.	Calculated Value.	Observed Value.	Other observed Values.	References.
H ₂	15.8	16.0 15.8 16.0 16.4	{ Olmstead, P. S. P. R. xx, p. 613 (1922). Davis and Goucher, P. R. x, p. 101 (1917). Foote and Mohler, 'Origin of Spectra,' p. 68. Franck, Knipping, and Kruger, <i>Ber. d. D. Phys. Ges.</i> xxi, p. 728 (1920) Also Franck, <i>Zeit. f. Phys.</i> xi, p. 160 (1922). Horton and Davies, Roy. Soc. Proc. xvii, p. 23 (1920). Also Davies, P. M. xiv, p. 797 (1923).
N	16.3	16.2 16.9 17.0	{ Duffendack, O. S. P. R. xx, p. 665 (1922). Foote and Mohler, J. O. S. A. iv, p. 49 (1920). Brandt, <i>Zeit. f. Phys.</i> viii, p. 32 (1921). Franck, <i>Loc. cit.</i>
O ₂	12.5	15.5	Foote and Mohler, J. O. S. A. iv, p. 49 (1920).
HCl	13.7*	13.8	13.7	{ Knipping, <i>Zeit. f. Phys.</i> vii, p. 328 (1921). Also Franck, <i>Loc. cit.</i>
HBr	13.5*	13.2	13.3	
HI	12.9*	12.8	12.7	
H ₂ O	13.2	13.0	Foote and Mohler, 'Origin of Spectra,' p. 188.
NH ₃	11.1		
He	24.5†	24.5	24.5 24.5	{ Franck and Knipping, <i>Zeit. f. Phys.</i> i, p. 320 (1920). Also Franck, <i>Loc. cit.</i> Horton and Davies, <i>Loc. cit.</i> Also Davies, <i>Loc. cit.</i>

* Born and Fajans, *loc. cit.*

† Lyman, *loc. cit.*

XCI. *On the Theory of X-Ray Absorption and of the Continuous X-Ray Spectrum.* By H. A. KRAMERS, Copenhagen*.

§ 1. *Definition of the problems and statement of the main results.*

THE origin of the absorption of homogeneous X-rays in matter may be traced to processes of two essentially different types. By the first of these the energy of the radiation is diminished as a consequence of processes of transference between two stationary states of the atoms, consisting in the removal of electrons from the interior of the atom (true absorption). By the second, the direction of propagation of the radiation is partly altered as a consequence of the reaction of the electrons in the atoms against the electrodynamic forces in the field of radiation (scattering). The mass-absorption coefficient may therefore be written in the well-known form

$$\frac{\mu}{\rho} = \frac{\tau}{\rho} + \frac{\sigma}{\rho}, \quad (1)$$

where μ is the coefficient of the observed absorption, τ the coefficient of the true absorption, and σ the coefficient of absorption through scattering, while ρ is the density. Except for light elements and short wave-lengths, τ is large compared with σ .

As well known, the observed absorption may with great approximation be considered as the sum of the absorbing actions of the individual atoms. The absorption due to a single atom may with great approximation be calculated from the observed value for μ for an element by multiplying by the atomic weight A and dividing by Avogadro's number M . Writing $\mu A/\rho M = \alpha_\mu$, $\tau A/\rho M = \alpha_\tau$, and $\sigma A/\rho M = \alpha_\sigma$, we have thus for the atomic absorption coefficient:

$$\alpha_\mu = \alpha_\tau + \alpha_\sigma, \quad (2)$$

where α_τ corresponds to the true absorption and α_σ to the scattering of the rays. The quantity α has the dimensions of an area, and can be interpreted in the following way: Each atom acts as a small sphere of cross section α , which absorbs completely all the rays which strike its surface. The quantity α may therefore, with Lenard's terminology, be called the "effective cross section."

* Communicated by Prof. N. Bohr.

The experimental results have shown* that α_μ with considerable accuracy may be represented by

$$\alpha_\mu = CN^k\lambda^l + D(N), \quad . \quad . \quad . \quad (3)$$

where N is the atomic number and λ the wave-length. C is a constant independent of N and λ , which takes different values on the different sides of the characteristic absorption limits K, L, \dots ; while D depends on N . For the exponent k , the investigators give values between 3.5 and 4; while for l they give values between 2.5 and 3. In general, the second term on the right side of (3) is small compared with the first. For light elements and short wave-lengths, however, the second term may become much larger; and here the experimental value for D agrees† for light elements more or less closely with the theoretical value for the scattering from the electrons deduced by J. J. Thomson‡:

$$D(N) = \frac{8\pi}{3} \frac{e^4 N}{m^2 c^4} = 0.54 \cdot 10^{-24} \cdot N, \quad . \quad . \quad . \quad (4)$$

which has also been confirmed by Barkla's § direct experiments on the amount of scattering from light elements. Richtmeyer ¶ represents for short wave-lengths the results of his absorption measurements with satisfactory accuracy by the formula

$$\alpha_\mu = CN^4\lambda^3 + D(N), \quad . \quad . \quad . \quad (5)$$

where C on the short wave-length side of the K limit has the value 0.0229 cm.^{-1} when λ is measured in cm. , while D for light elements does not differ much from the theoretical scattering coefficient (4). For heavier elements, D is several times larger. Also the scattering for these elements is several times larger than would correspond to (4), as was directly shown by Barkla and Miss Dunlop ¶, and as would be expected from the theory. It cannot be assumed, however, that Richtmeyer's D term just corresponds to the scattering coefficient α_σ , because the theory as well as the experiment

* W. H. Bragg and S. Peirce, *Phil. Mag.* xxviii. p. 626 (1914). A. Hull and M. Rice, *Phys. Rev.* viii. p. 326 (1916). R. Glocker, *Phys. Zeitschr.* xix. p. 71 (1918). E. A. Owen, *Proc. Roy. Soc.* xciv. pp. 339 and 510 (1918). Siegbahn and Wingårdh, *Phys. Zeitschr.* xxi. p. 83 (1920). F. K. Richtmeyer, *Phys. Rev.* xvii. p. 13 (1921). K. A. Wingårdh, *Zeitschr. f. Phys.* viii. p. 365 (1922), and Dissertation, Lund, 1923.

† Hull and Rice, *loc. cit.*

‡ J. J. Thomson, 'Conduction of Electricity through Gases,' p. 326 (Cambridge, 1907).

§ C. G. Barkla, *Phil. Mag.* vii. p. 543 (1904).

¶ F. K. Richtmeyer, *loc. cit.*

¶ Barkla and Dunlop, *Phil. Mag.* xxxi. p. 222 (1916).

show that the scattering for the heavier elements increases with increasing wave-length. Wingårdh, in his dissertation*, arrives at results which for short wave-lengths ($\lambda < 0.35$ Å.) and elements with atomic number larger than 10 are represented by formula (5), where C on the short wave-length side of the K absorption limit has the value 0.0244 and on the long wave-length side a value about 5 to 7 times smaller, while D has the form $3 \cdot 10^{-26} N^2$.

The continuous X-ray spectrum has in the course of the last years been investigated by a number of physicists†. The problem is here to determine how, for a given tension on the tube and a given anticathode material, the energy in the continuous spectrum is distributed among different frequencies. As well known, this distribution varies with the angle which the direction in which the X-rays are observed makes with the direction of the cathode-rays‡. This distribution, especially for high tension, is not exactly symmetrical with regard to a plane perpendicular to the cathode-rays—a phenomenon which certainly may be ascribed to a kind of Doppler effect§. Kühlenkampff|| has recently made an extensive investigation of the continuous X-ray spectrum excited by rather low potentials (below 12,000 volts), and observed at an angle of about 90 degrees with the direction of the cathode rays. Calling the intensity of the part of the spectrum lying between ν and $\nu + d\nu$ by $I_\nu d\nu$, and denoting the quantum-theory limit of the continuous spectrum by ν_0 , which is related to the applied voltage V by the Einstein relation

$$h\nu_0 = Ve, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where e is the charge of the electron and h Planck's constant, Kühlenkampff represents his results rather closely by the formula

$$I_\nu = C\{N(\nu_0 - \nu) + N^2b\}, \quad . \quad . \quad . \quad (7)$$

holding for all values of $\nu < \nu_0$, while for $\nu > \nu_0$ the intensity I_ν is equal to zero. N represents the atomic number of the element of the anticathode. The constant b is about equal

* Loc. cit.

† A most valuable survey of the experimental and theoretical work published until the fall of 1920 is given by D. L. Webster, "Problems of X-ray Emission," Bulletin of the National Research Council, vol. i. Part 7, Dec. 1920 (Washington), where also literature references are given. See also E. Wagner, *Jahrb. d. Rad. u. Elektr.* xvi. p. 190 (1919).

‡ C. E. Wagner, *Phys. Zeitschr.* xxi. p. 621 (1920).

§ Cf. A. Sommerfeld, *Phys. Zeitschr.* x. p. 969 (1909).

|| H. Kühlenkampff, *Ann. d. Phys.* lxi. p. 548 (1923).

to $2.5 \cdot 10^{15}$ (if ν is measured in cm^{-1}). Kühlenkampff emphasizes that the sharp bend in the intensity curve claimed by formula (7) is rather smooth in the experiment. The absolute value of C has not been determined by Kühlenkampff, but can with some accuracy be found from experiments on the total X-ray emission under given conditions. The formulæ for the continuous X-ray spectrum proposed by Webster* agree in the main with formula (7).

The object of the present paper is to show how it is possible to account theoretically for the main features of the phenomena of X-ray absorption and continuous X-ray emission discussed above. The explanation of these phenomena may be traced back to the determination of the radiation processes which may occur when a free electron of given velocity approaches a positive nucleus with given charge. The latter problem cannot at the present state of the quantum theory of radiation be solved in detail, but it will be shown how an application of the ideas underlying Bohr's correspondence principle enables us to obtain an approximative solution, which leads to very satisfactory results when applied to X-ray absorption and to the continuous X-ray spectrum. Thus the theory leads, in first approximation, to the following formula for the atomic true absorption coefficient:

$$\alpha_{\tau} = CN^4\lambda^3, \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where C , for wave-lengths shorter than the K limit, is given by

$$C = g \frac{64\pi^4}{3\sqrt{3}} \frac{e^{10}m}{c^4h^6} = g \cdot 0.0104 \quad . \quad . \quad . \quad (9)$$

(e and m charge and mass of electron, c velocity of light, h Planck's constant). In this formula g is a numerical factor of the same order of magnitude as 1, whereas the experimental value, as mentioned, is equal to 0.023 to 0.025 †.

* D. L. Webster, Phys. Rev. ix. p. 220 (1917).

† In the 11th chapter of 'Conduction of Electricity through Gases' J. J. Thomson has, by means of the classical theory of electrons, derived an expression for the absorption of X-rays on the basis of Stokes' æther pulse theory, by calculating the work which an electromagnetic pulse conveys to an electron which can perform harmonic oscillations round a position of equilibrium and which is originally at rest. The result depends essentially on the form of the pulse. If the pulse is assumed to be a "double" pulse—i. e., if its form is such that a short time-period τ in which the electric force has one direction is followed by a period of the same length in which this force has the same magnitude but the opposite direction—the resultant absorption will be proportional

For the continuous X-ray spectrum, on the other hand, the following expression is obtained for the energy between ν and $\nu + d\nu$ radiated in all directions :

$$I_\nu = i \frac{8\pi}{3\sqrt{3}l} \frac{e^2 h}{c^3 m} \cdot N(\nu_0 - \nu) \sim i \cdot 5 \cdot 10^{-50} N(\nu_0 - \nu), \quad (10)$$

where i is the number of electrons striking the target in unit time, while l is a numerical factor of the order of magnitude 6. The formula (10) is very similar to the experimental formula (7) *. Moreover, the numerical value of the coefficient is in satisfactory agreement with the experiments on the total efficiency of X-ray tubes.

§ 2. *The connexion between the probability of absorption of radiation and the probability of emission of radiation due to the capture of a free electron.*

On the quantum theory of radiation, the process of the absorption of X-rays must be considered as governed by the laws of probability in much the same way as absorption and emission of radiation are treated in Einstein's theory of temperature radiation †. Thus we must assume that when

to the cube of τ . Identifying τ with the period λ/c of a beam of homogeneous X-rays, and the natural frequency of the electron with the frequency of the K absorption limit, A. H. Compton (Phys. Rev. xiv. p. 249 (1919)) has shown that Thomson's formula can be written in the form.

$$\alpha = 32\pi^7 e^{10} m / c^4 h^6 \cdot N \lambda^3,$$

which differs only from that given by (9) by the value of the numerical factor.

An attempt to account for the observed laws of absorption on the basis of our present views of the nature of X-rays and of the structure of the atom has recently been made by L. de Broglie (*Journ. de Phys.* iii. p. 33, 1922). Although this author arrives at a result which, just as Compton's formula, differs from (9) only by the value of the numerical factor, his treatment of the problem, which at all points differs essentially from that followed in this paper, seems not to be consistent with the way in which the quantum theory at present is applied to atomic problems. (Compare *Physikalische Berichte*, iv. p. 496, 1923.)

* For earlier attempts to develop a theory of continuous X-ray emission, compare E. March, *Physik. Zeitschr.* xxii. pp. 209, 429 (1921); Bergen Davis, *Phys. Rev.* ix. p. 64 (1917); H. Brillouin, *Comptes Rendus*, clxx. p. 274 (1920); H. Behnken, *Zeitschr. f. Phys.* iv. p. 241 (1921).

† A. Einstein, *Phys. Zeitschr.* xviii. p. 127 (1917).

an atom is placed in a beam of homogeneous X-rays there exists a certain probability proportional to the intensity of the rays that within a given time-interval one of the electrons—for instance, a K electron—in the interior of the atom is expelled and leaves the atom with a velocity v determined by the Einstein relation :

$$h\nu = W + \frac{1}{2}mv^2, \quad . \quad . \quad . \quad . \quad (11)$$

where ν is the frequency of the incident rays and W the work necessary for the complete removal of the electron from the atom. The formula holds with neglect of terms of the order $\left(\frac{v}{c}\right)^2$ and higher.

The quantum theory, in its present state, tells nothing about the mechanism of absorption and does not therefore permit the direct calculation of the probability that an absorption process may occur. By imagining, however, a thermodynamical equilibrium between atoms and free electrons on the one hand and temperature radiation in space on the other, it is possible to establish a relation between this probability of absorption and the probability of the inverse process, which consists in the binding of a free electron of velocity v by an atom in which a K electron is missing—a process which will be accompanied by the emission of radiation of frequency ν . The relation thus obtained will be quite analogous to the relation between the probability of the occurrence of a spontaneous emission process and of an absorption process, obtained by Einstein in his above-mentioned theory of temperature radiation.

Let us for the sake of simplicity assume that there is a single neutral atom in a vessel of volume V , in which the temperature is equal to T . Then, according to Boltzmann's principle, the probability P_n that the atom is in its neutral normal state has a proportion to the probability $P_v dv$ that a certain electron—for instance, a K electron—is missing and moves freely outside the ionized atom with a velocity lying between v and $v + dv$ will be given by

$$P_n : P_v dv = ah^3 e^{\frac{h\nu}{kT}} : 4\pi V m^3 v^2 dv. \quad . \quad . \quad . \quad (12)$$

ν has the same significance as in (11); ah^3 represents the *a priori* probability for the electron under consideration

to be bound in the atom *, so that a is a numerical factor ; k is Boltzmann's constant †.

We will now find a mathematical expression for the fact that the proportion given by (12) is not changed by the interaction with the field of radiation. For that purpose we will introduce—besides the effective cross-section α_r , governing (in the way described, p. 836) the true absorption of rays by the normal atom leading to an expulsion of the electron—another effective cross-section β peculiar to the atom in the ionized state under consideration, which has the following significance:—The probability that, by a collision with the free electron, the ionized atom will bind this electron in its interior, accompanied by the spontaneous emission of a radiation quantum $h\nu$, is such that if the atom is imagined as a sphere of cross-section β the free electron will be bound by the atom if, and only if, it strikes the surface of this sphere. β is clearly seen to be a function of the velocity v and to depend on what kind of electron is missing in the ionized atom. The probability that the free electron moving with velocity v in a time-interval dt will be bound in the atom is obviously equal to

$$Q_{i \rightarrow n} dt = \frac{\beta v}{V} dt. \quad . \quad . \quad . \quad (13)$$

On the other hand, the probability that under the influence of the field of radiation the neutral atom in a time-interval dt will be ionized in such a way that the electron expelled has a velocity lying between v and $v + dv$ is equal to

$$Q_{n \rightarrow i} dt dv = \alpha_r \frac{\rho(v, T) c dt}{h\nu} \frac{dv}{v} dv, \quad . \quad . \quad . \quad (14)$$

where $\rho(v, T) dv$ represents the energy in the radiation field the frequency of which lies between ν and $\nu + d\nu$. Assuming that the temperature is not so high that the temperature radiation will have a sensible influence on the processes

* For instance, in an atom consisting of a nucleus and a single electron, where the stationary states are characterized in the well-known way by an integer n , the *a priori* probability of the n th state is equal to $n(n+1)h^2$. (Compare Bohr, 'On the Quantum Theory of Line Spectra,' Copenhagen Academy (1918), Part ii, p. 76.)

† This method is seen to be essentially the same as that by means of which the chemical constant of gases and vapours may be theoretically derived, as well as the laws governing the emission of electrons from hot metals. In the treatment of these problems, however, a is often put equal to 1, an assumption for which in general no sufficient reason can be given. Cf. W. Schottky, *Phys. Zeitschr.* xxii, p. 1 (1921).

by which the free electron will be bound by the ionized atom (Einstein's "negative Einstrahlung"), and assuming for the function $\rho(\nu, T)$ in the region of this temperature with sufficient approximation *

$$\rho(\nu, T) = \frac{8\pi h\nu^3}{c^3} e^{-\frac{h\nu}{kT}}, \quad (15)$$

the thermodynamical claim that the probability proportion (12) is not changed by the interaction with the field of radiation assumes the form

$$P_n Q_{n \rightarrow i} = P_i Q_{i \rightarrow n}; \quad (16)$$

or, making use of (13), (14), and (15),

$$ah^3 e^{\frac{h\nu}{kT}} \cdot \alpha_\tau \frac{8\pi h\nu^3}{c^3} e^{-\frac{h\nu}{kT}} \frac{c}{h\nu} \frac{d\nu}{d\nu} = 4\pi V m^3 v^2 \cdot \frac{\beta v}{V},$$

or, observing that by means of (11) we have $\frac{d\nu}{d\nu} = \frac{mv}{h}$,

$$\alpha_\tau = \frac{m^2 v^2 c^2}{2ah^2 v^2} \beta, \quad (17)$$

in which formula c and v are connected by the relation (11).

§ 3. *The classical radiation from a free electron deflected by a positive nucleus.*

We shall now seek an expression for β , *i. e.* the efficient cross-section of the ionized atom with regard to free electrons which, by the emission of radiation, are bound by the atom in an orbit in its interior of the type considered. The quantum theory gives no information regarding the details of such an emission process; it claims only that the radiation is monochromatic and that the energy emitted amounts to a quantum $h\nu$. The only procedure which offers itself at present seems to consist in estimating the statistical result of a great number of such emission processes by investigating—in a way suggested by Bohr's correspondence principle—the radiation which on the classical electron theory would be emitted by the free electrons in consequence of the change in motion produced by the forces arising from the electric particles in the atom. In view of the approximative character of the results which may be obtained in this way, we are led in the treatment of

* These assumptions do not, as will follow from a comparison with Einstein's cited paper, contain any restriction as regards the final result.

this problem to introduce a simplification which makes the electrodynamical problem much easier. Thus we shall confine ourselves to the consideration of the radiation which will be emitted by a free electron which "collides" with a single nucleus of charge Ne , *i.e.* which on its way approaches the nucleus so closely that its motion undergoes a considerable change.

Let the velocity of the electron before the collision be v , and let ρ designate the perpendicular distance of the nucleus from the original path of the electron. Disregarding the variation of the mass of the electron with its velocity, and assuming that the total loss of energy due to radiation is small compared with the kinetic energy $\frac{1}{2}mv^2$, the electron will describe a hyperbolical orbit with the nucleus at one of the foci. If the angle of deflexion of the electron is denoted by $\pi - 2\phi_0$, we have *

$$\tan \phi_0 = \frac{mpv^2}{Ne^2} \quad . \quad . \quad . \quad . \quad . \quad (18)$$

The amount of energy lost in unit time by the electron in the form of electromagnetic radiation is given by †

$$\frac{dR}{dt} = \frac{2e^2}{3c^3} j^2, \quad . \quad . \quad . \quad . \quad . \quad (19)$$

where j denotes the acceleration of the electron. The total loss of energy R due to radiation is found immediately by integrating the expression (19) over the time. If we call the eccentricity ϵ , and if we describe the position of the electron in the plane of its orbit by means of polar coordinates r and ϕ , where r is the distance from the nucleus and ϕ the angular distance from the major axis, we have

$$\begin{aligned} \frac{1}{r} &= \frac{1 - \epsilon \cos \phi}{p \tan \phi_0}, \quad r^2 \dot{\phi} = pr, \quad \epsilon = \sec \phi_0, \quad j = \frac{Ne^2}{mr^2}, \\ R &= \int_{-\infty}^{+\infty} \frac{2e^2}{3c^3} j^2 dt = \frac{2N^2e^6}{3c^3m^2} \int_{-\infty}^{+\infty} \frac{dt}{r^4} = \frac{2N^2e^6}{3c^3m^2pv} \int_{\phi_0}^{2\pi - \phi_0} \frac{d\phi}{r^2} \\ &= \frac{2N^4e^{10}}{3c^3m^4p^5v^5} \int_{\phi_0}^{2\pi - \phi_0} (1 - \epsilon \cos \phi)^2 d\phi, \quad . \quad . \quad . \quad . \quad . \quad (20) \\ \int_{\phi_0}^{2\pi - \phi_0} (1 - \epsilon \cos \phi)^2 d\phi &= (2\pi - 2\phi_0)(1 + \sec^2 \phi_0/2) + 3 \tan \phi_0. \\ & . \quad . \quad . \quad . \quad . \quad (21) \end{aligned}$$

* Compare, for instance, E. Rutherford, Phil. Mag. xxi. p. 669 (1911).

† Compare, for instance, H. A. Lorentz, 'The Theory of Electrons,' p. 52 (2nd ed.).

Considering first the case where ϕ is a small angle, i. e.,

$$\tan \phi_0 = \frac{mpe^2}{Ne^2} \ll 1, \quad . \quad . \quad . \quad . \quad (22)$$

the integral (21) is in first approximation equal to 3π , and with the same approximation the radiated energy becomes equal to

$$R = \frac{2\pi N^4 e^{10}}{c^3 m^4 \gamma^5 v^5} \quad . \quad . \quad . \quad . \quad (23)$$

This energy is emitted as an electromagnetic æther pulse, the form of which can be found in the well-known way from the way in which the acceleration j changes with the time as regards direction and magnitude. In the case just considered, where the angle ϕ_0 is assumed to be small, the orbit of the electron will, especially in the neighbourhood of the nucleus, differ only little from a *parabolic Keplerian orbit*. On account of this, the investigation of the form of the pulse, and especially of the distribution of the energy emitted among different frequencies which will have special interest for us, can—for all values of N , p , and v for which the derivation of formula (23) is justified—be reduced to the determination of the two functions which for one special parabolic orbit express the variation of the two components of the acceleration with the time.

Considering thus a parabolic Keplerian orbit for which the shortest distance between electron and nucleus is equal to $\frac{1}{2}$, and for which the angular momentum mpe of the electron with respect to the nucleus is equal to m , so that $Nc^2 m=1$, the polar coordinates r and ϕ and the time t are simply expressed in terms of an auxiliary variable z by means of the formula :

$$t = \frac{1}{2} \left(\frac{z^3}{3} + z \right), \quad r = \frac{1+z^2}{2}, \quad \cos \phi = -\frac{1-z^2}{1+z^2}, \quad \sin \phi = \frac{2z}{1+z^2} \quad . \quad . \quad . \quad (24)$$

The components of the acceleration perpendicular to and parallel to the axis will be given by

$$j_{\text{perp.}} = -\frac{\sin \phi}{r^2} = -\frac{8z}{(1+z^2)^3}, \quad j_{\text{par.}} = -\frac{\cos \phi}{r^2} = \frac{4(1-z^2)}{(1+z^2)^3} \quad (25)$$

In order to find how much of the energy radiated belongs to the different frequencies *, the functions (25) must be

* Cf. for instance J. H. Jeans, Phil. Mag. xx. p. 642 (1910).

developed in Fourier integrals:

$$j_{\text{perp.}}(t) = \int_0^\infty \phi(\gamma) \sin \gamma t d\gamma, \quad j_{\text{par.}}(t) = \int_0^\infty \psi(\gamma) \cos \gamma t d\gamma, \quad (26)$$

where

$$\phi(\gamma) = \frac{1}{\pi} \int_{-\infty}^{+\infty} j_{\text{perp.}}(\tau) \sin \gamma \tau d\tau, \quad \psi(\gamma) = \frac{1}{\pi} \int_{-\infty}^{+\infty} j_{\text{par.}}(\tau) \cos \gamma \tau d\tau, \quad (27)$$

and where in the two last integrals the time is denoted by τ .

If in (27) we introduce z as integration variable by means of (24) and (25), we find, after some calculation,

$$\phi(\gamma) = \gamma i^{1/3} 3^{-1/2} H_{1/3}^{(1)}(i\gamma/3), \quad \psi(\gamma) = \gamma i^{5/3} 3^{-1/2} H_{2/3}^{(1)}(i\gamma/3). \quad (28)$$

In these formulæ $H_\rho^{(1)}(x)$ denotes the Hankel function of the first kind and of the order ρ *: from the properties of this function it will be seen that the given expressions are real for real values of γ . For small values of γ we have convergent expansions, the first two terms of which are given by

$$\phi(\gamma) = 0.89\gamma^{2/3} - 0.41\gamma^{4/3} + \dots,$$

$$\psi(\gamma) = 0.82\gamma^{1/3} - 0.22\gamma^{5/3} + \dots,$$

while for big values of γ we have asymptotic expansions which begin as follows:

$$\phi(\gamma) = \sqrt{\frac{2\gamma}{\pi}} e^{-\frac{\gamma}{3}} \left(1 - \frac{5}{24\gamma} + \dots\right),$$

$$\psi(\gamma) = \sqrt{\frac{2\gamma}{\pi}} e^{-\frac{\gamma}{3}} \left(1 + \frac{7}{24\gamma} - \dots\right).$$

Fig. 1 gives a graphical representation of the functions ϕ and ψ .

For the total energy emitted we have

$$R = \frac{2e^2}{3c^3} \int_{-\infty}^{+\infty} (j_{\text{perp.}}^2 + j_{\text{par.}}^2) dt = \frac{2\pi e^2}{c^3} \quad (29)$$

On the other hand we have

$$\int_{-\infty}^{+\infty} (j_{\text{perp.}}^2 + j_{\text{par.}}^2) dt = \pi \int_0^\infty (\phi^2(\gamma) + \psi^2(\gamma)) d\gamma. \quad (30)$$

* $H_p^{(1)}(x) = \frac{i}{\sin p\pi} \{e^{-p\pi i} J_p(x) - J_{-p}(x)\}$ (p not integer), where $J_p(x)$ is the ordinary Bessel function. This definition has been proposed by N. Nielsen, 'Handbuch der Zylinderfunktionen' (Leipzig, 1904). See further the very useful formulæ in Jahnke and Emde's *Funktionentafeln* (Leipzig, 1909).

We may therefore say that the relative amount of the radiated energy the frequency of which, multiplied by 2π , lies between γ and $\gamma + d\gamma$ is given by

$$P(\gamma)d\gamma = \frac{1}{3}(\phi^2(\gamma) + \psi^2(\gamma))d\gamma, \quad \int_0^\infty P(\gamma)d\gamma = 1. \quad (31)$$

Fig. 1.

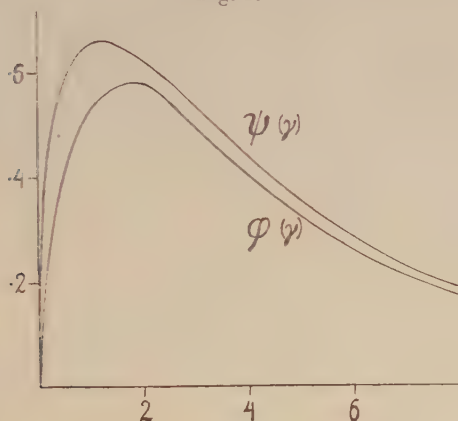


Fig. 2.

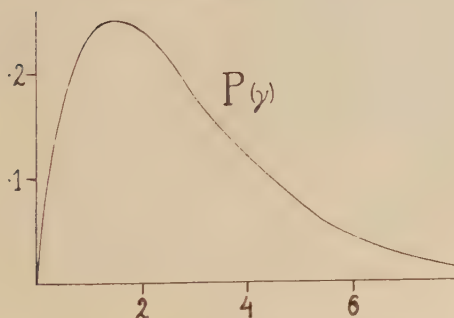


Fig. 2 gives a graphical representation of the function $P(\gamma)$, which has its maximum value in the neighbourhood of $\gamma = 1.5$. In this connexion the value of the following integral may be noted, which follows directly from a general integration formula holding for all functions which, just as the Hankel functions, satisfy the Bessel differential equation* :

$$\int_0^\infty \frac{P(\gamma)}{\gamma} d\gamma = \frac{4}{\pi\sqrt{3}}. \quad \dots \dots \dots (32)$$

* Whittaker and Watson, 'Modern Analysis,' 3rd edition, p. 381, ex. 18; Jahnke and Emde, *loc. cit.* p. 166.

In the general case the shortest distance of the electron in its parabolic orbit from the nucleus is equal to $\frac{mp^2v^2}{2Ne^2}$, while the angular momentum of the electron round the nucleus is equal to mpv . Here it will obviously again be the function $P(\gamma)$ which tells us how the energy is distributed on the different frequencies. We need only to calculate which value of the frequency ν corresponds to a given value of γ . Now it is easily seen that the angular velocity in the pericentrum holding for the parabolic orbit defined by (24) is equal to 4, while for the general parabolic orbit it is equal to $\frac{4N^2e^4}{m^2p^3r^3}$. We may therefore directly put

$$\gamma = 2\pi\nu \frac{m^2p^3v^3}{N^2e^4}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

It is of interest to remark that, for two parabolic orbits corresponding to the same angular momentum, *i. e.* to the same value of pv , the energy in the radiation lying between ν and $\nu + d\nu$ is the same. This follows directly from the circumstance that in (23) as well as in (33) p and v occur only in the combination pv .

In the foregoing we have established the formulæ by which is fixed the character of the energy-radiation which on the classical theory would take place from a parabolic orbit. In order that these formulæ hold, three conditions must be fulfilled :

- (a) In order that the orbit can be represented with sufficient accuracy as a parabola, the condition (22) must be fulfilled.
- (b) The total amount of energy radiated on the classical theory must be small compared with the kinetic energy of the electron :

$$\frac{2\pi N^4e^{10}}{c^3m^4p^5r^5} \ll \frac{1}{2}mv^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

- (c) In order that the application of Newtonian mechanics may be justified, the velocity of the electron must, even in the point where it is largest, *i. e.* in the pericentrum, be small compared with the velocity of light :

$$\frac{2Ne^2}{mpe} \ll c. \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

These conditions do not contradict each other. In fact, putting

$$\frac{mpv^2}{Ne^2} = A, \quad \frac{4\pi N^4 e^{10}}{c^3 m^5 p^5 v^7} = B, \quad \frac{2Ne^2}{cmpv} = C, \quad \dots \quad (36)$$

where A, B, and C are numerical quantities, we have

$$A^2 B = \frac{\pi}{2N} C^3, \quad \dots \quad (37)$$

showing that if conditions (a) and (b) are fulfilled ($A \ll 1$, $B \ll 1$), the condition (c) will in general also be satisfied.

We will now investigate the case where the angle ϕ defined by (18) differs only little from $\pi/2$, *i. e.*

$$\tan \phi_0 = \frac{mpv^2}{Ne^2} \gg 1. \quad \dots \quad (38)$$

This corresponds to a hyperbolic orbit of the electron where the angle between the asymptotes is almost equal to 180° , *i. e.* where the electron describes an almost *rectilinear orbit*. The integral (21) reduces in this case in first approximation to $\pi \sec^2 \phi_0/2$, and the radiated energy (20) becomes equal to

$$R = \frac{\pi N^2 e^6}{3c^3 m^2 p^3 v}. \quad \dots \quad (39)$$

Just as in the case of a nearly parabolical orbit, the determination of the distribution of this energy for all values of N , p , and v satisfying (38) can be reduced to the determination of this energy distribution for one special *rectilinear orbit*. Considering thus an electron passing a positive nucleus at a distance $p \gg 1$ and with a velocity numerically equal to p , the components of the acceleration of the electron perpendicular to and parallel to its path, considered as a function of the time, are respectively given by

$$j'_{\text{perp.}} = (1+t^2)^{-3/2}, \quad j'_{\text{par.}} = t(1+t^2)^{-3/2}, \quad \dots \quad (40)$$

if the nuclear charge is chosen such that Ne^2/m is numerically equal to p^2 .

In analogy with our former procedure, the functions (40) must be developed in Fourier integrals:

$$j'_{\text{perp.}}(t) = \int_0^\infty \phi'(\gamma) \cos \gamma t \, d\gamma, \quad j'_{\text{par.}}(t) = \int_0^\infty \psi'(\gamma) \sin \gamma t \, d\gamma, \quad \dots \quad (41)$$

where

$$\phi'(\gamma) = \frac{1}{\pi} \int_{-\infty}^{+\infty} j'_{\text{perp.}}(\tau) \cos \gamma \tau \, d\tau, \quad \psi'(\gamma) = \frac{1}{\pi} \int_{-\infty}^{+\infty} j'_{\text{par.}}(\tau) \sin \gamma \tau \, d\tau, \quad \dots \quad (42)$$

where in the latter integrals the time is denoted by τ . Introducing (40) we find the expressions :

$$\phi'(\gamma) = -\gamma H_1^{(1)}(i\gamma), \quad \psi'(\gamma) = i\gamma H_0^{(1)}(i\gamma), \quad . \quad (43)$$

involving the Hankel functions of the first kind of the order 1 and 0. For γ small we have the convergent expansions :

$$\begin{aligned} \phi' &= \frac{2}{\pi} + \frac{\gamma^2}{\pi} \left(\log \frac{\zeta\gamma}{2} - \frac{1}{2} \right) + \dots \\ \psi' &= -\frac{2}{\pi} \gamma \log \frac{\zeta\gamma}{2} + \frac{\gamma^3}{2\pi} \left(1 - \log \frac{\zeta\gamma}{2} \right) + \dots \\ &(\log \zeta = 0.5772\dots). \end{aligned}$$

For large values of γ we have the asymptotic expansions :

$$\begin{aligned} \phi'(\gamma) &= \sqrt{\frac{2\gamma}{\pi}} e^{-\gamma} \left(1 + \frac{3}{8}\gamma + \dots \right), \\ \psi'(\gamma) &= \sqrt{\frac{2\gamma}{\pi}} e^{-\gamma} \left(1 - \frac{1}{8}\gamma + \dots \right). \end{aligned}$$

Fig. 3 gives a graphical representation of the functions ϕ' and ψ' . For the total energy emitted we have :

$$R = \frac{2e^2}{3c^3} \int_{-\infty}^{+\infty} (j_{\text{perp.}}'^2 + j_{\text{par.}}'^2) dt = \frac{\pi e^2}{3c^3}.$$

With reference to (30) we may therefore say that the relative amount of the radiated energy the frequency of which, multiplied by 2π , lies between γ and $\gamma + d\gamma$ is given by

$$P'(\gamma) d\gamma = 2(\phi'^2 + \psi'^2) d\gamma, \quad \int_0^\infty P'(\gamma) d\gamma = 1. \quad (44)$$

Fig. 4 gives a graphical representation of $P'(\gamma)$.

In general, for an arbitrary set of values for N , ρ , and v satisfying (38), the energy distribution is again given by (44), if γ is related to the frequency ν by the relation

$$\gamma = 2\pi\nu \frac{\rho'}{v}. \quad . \quad . \quad . \quad . \quad . \quad (45)$$

In order that these formulæ can be applied, three conditions must be fulfilled:

(a) The relation (38) must be fulfilled.

Fig. 3.

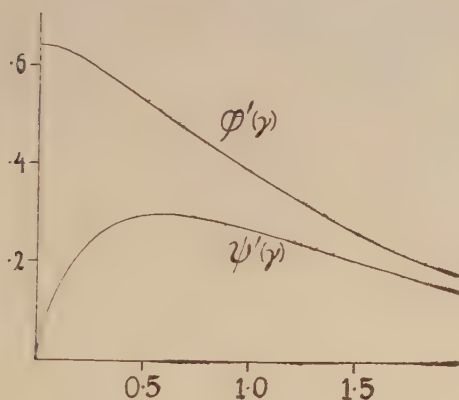
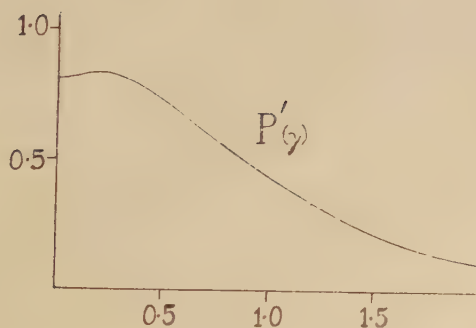


Fig. 4.



(b) The total amount of energy radiation must be small compared with the kinetic energy of the electron :

$$\frac{\pi N^2 e^6}{3c^3 m^2 \rho^3 v} \leq \frac{1}{2} m v^2. \quad . \quad . \quad . \quad . \quad (46)$$

(c) The velocity of the electron v must be small compared with the velocity of light.

Putting

$$\frac{Ne^2}{mpv^2} = A', \quad \frac{2\pi N^2 e^6}{3c^3 m^3 p^3 v^3} = B', \quad \frac{v}{c} = C', \quad . \quad . \quad (47)$$

where A' , B' , and C' are numerical quantities, we see that

$$A'^3 C'^3 = \frac{3N}{2\pi} B', \quad . \quad . \quad . \quad (48)$$

showing that if the conditions (a) and (c) are fulfilled, the condition (b) will always be satisfied.

§ 4. *The quantum theory radiation from a free electron colliding with a positive nucleus.*

With reference to the application of the quantum theory to radiation problems, we will assume that a free electron which collides with a positive nucleus may perform a transition to a stationary state of motion of less energy, accompanied by the emission of a quantum $h\nu$ of monochromatic radiation. In the latter state the electron may either still be free—i.e. the electron may after the collision leave the nucleus with any velocity smaller than its original velocity—or the collision will result in the binding of the electron in one of the discrete series of elliptical or circular stationary states known from Bohr's theory of atomic structure. The statistical result of a large number of collisions with free electrons of the same velocity will therefore be the emission of a continuous spectrum, extending from very small frequencies to a limiting frequency ν_0 determined by $h\nu_0 = \frac{1}{2}mv^2$, and of a spectrum of discrete lines, extending from this limit towards larger frequencies*. The line of highest frequency will correspond to a transition by which the electron is bound in a one-quantum orbit. In view of the correspondence principle, we are led to expect that the intensity distribution in this spectrum may be estimated from the intensity distribution in the radiation which the colliding electrons would emit on the classical theory. Thus with reference to the applications of the correspondence principle to series spectra, we should expect that every possible quantum transition corresponds to a certain frequency present in the motion of the electron, and that the probability for the occurrence of a transition process is closely connected with the amount of energy in the radiation which on the classical theory is correlated with the corresponding frequency.

* Cf. N. Bohr, 'On the Quantum Theory of Line Spectra,' Copenhagen Academy, 1918, Part ii, p. 99.

Here we meet immediately the question, Which frequency in the motion corresponds to a given transition? In the present case the answer cannot be given in the same unambiguous way as was possible in the quantum theory of simple and multiple periodic systems, where the motion can be analysed in discrete harmonic components. If we confine ourselves, however, for the moment to those transitions where the electron is also free after the radiation process, the very simple assumption offers itself that the corresponding frequency is just equal to the frequency of the emitted radiation. As well known, such is not in general true for simple or multiple periodic systems where we have to do with discrete stationary states, but here there is at first sight nothing which prevents the introduction of such an assumption. It leads us immediately to the following way of estimating the probability for a transition by which the electron by performing a transition from one free state to another radiates a frequency ν . Let again the nuclear charge be denoted by Ne , the velocity of the electron before the collision by v , and the distance from the nucleus to the original path of the electron by ρ , and let us suppose that the condition (22) is fulfilled. According to the formulæ (23), (31), and (33), the energy which on classical electrodynamics would be sent out in the form of radiation with frequencies lying between ν and $\nu + d\nu$ from a great number s of collisions of the same type will be equal to

$$s \cdot \frac{2\pi N^4 e^{10}}{c^3 m^4 \rho^5} P(\gamma) \frac{d\gamma}{d\nu} d\nu = s \cdot \frac{4\pi^2 N^2 e^6}{c^3 m^2 \rho^2} P\left(2\pi\nu \frac{\rho^3 v^3 m^2}{N^2 e^4}\right) d\nu. \quad (49)$$

Denoting, on the other hand, by $q(\nu)d\nu$ the probability that a collision of the type considered gives rise to the emission of a radiation with frequency between ν and $\nu + d\nu$, the correspondence principle leads us to the estimation that $s \cdot q(\nu)h\nu d\nu$ is equal to the expression (49). We have of course not the least reason to expect that these two expressions will be exactly equal: thus we are, from the quantum theory of simple and multiple periodic systems, familiar with the idea that the initial state in a transition process is not sufficient in itself to determine the quantities which are characteristic of the process*.

* In this connexion it may be noted that a further support for the validity of our estimation may perhaps be derived in the case of transitions by which the angular momentum of the electron is not changed, since (as it has been remarked on p. 848) all nearly parabolic motions with the same angular momentum give rise to the same energy distribution in the classical radiation.

It seems difficult, however, at the present time to give a rational estimation of the quantity $s \cdot q(\nu) h\nu d\nu$ which may be regarded as more exact than that given above. We shall therefore write

$$q(\nu) h\nu d\nu \sim \frac{4\pi^2 N^2 e^6}{c^3 m^2 p^2 v^2} P \left(2\pi\nu \frac{p^3 v^3 m^2}{N^2 e^4} \right) d\nu, \quad . \quad . \quad (50)$$

remembering that the \sim sign only means a first approximation.

Until now we have considered the case where mpv^2/N^2e^2 is small compared with unity (condition (22)). If, on the other hand, this quantity is large compared with unity (condition (38)) we have to apply the formulæ (39), (44), and (45) holding for the energy distribution in the radiation from a nearly rectilinear orbit, and an easy calculation shows that (50) must be replaced by

$$q(\nu) h\nu d\nu \sim \frac{2\pi^2 N^2 e^6}{3c^3 m^2 p^2 v^2} P' \left(2\pi\nu \frac{p'}{v} \right) d\nu. \quad . \quad . \quad (51)$$

The assumptions (50) and (51) lead to a definite theory for the continuous X-ray spectrum which will be considered in §6. Here we will proceed by putting the further question: How large will the probability be that the electron under consideration radiates so much energy that the collision results in its binding in one of the discrete stationary orbits round the nucleus? As mentioned above, the emission spectrum resulting from such collisions will consist of separate lines, and there can be no question of a simple correspondence with the frequencies occurring in the original motion of the electron. It is tempting, nevertheless, to extend here the considerations on which (50) and (51) were based, and to assume that a certain frequency interval in the radiation emitted on the classical theory corresponds with a process by which the electron is bound in a certain stationary state. The following way of estimating the magnitude of the corresponding interval immediately suggests itself. The energy with which the electron is bound by the nucleus in the n th stationary state is given by

$$W = \frac{2\pi^2 N^2 e^4 m}{n^2 h^2}, \quad . \quad . \quad . \quad (52)$$

which value has to be introduced in the expression (11) for the frequency emitted by the electron which is being bound. We will therefore assume that the corresponding

frequency interval can be approximately represented by

$$\Delta\nu \sim \frac{2\pi^2 N^2 e^4 m}{h^3} \left(\frac{1}{(n-\frac{1}{2})^2} - \frac{1}{(n+\frac{1}{2})^2} \right) \sim \frac{4\pi^2 N^2 e^4 m}{h^3 n^3}. \quad (53)$$

Denoting the probability for the occurrence of a process by which the originally free electron is bound in the n th quantum state by q_n , we can thus write approximately :

$$\begin{aligned} q_n h\nu &= \frac{4\pi^2 N^2 e^6}{c^3 m^2 p^2 v^2} P \left(2\pi\nu \frac{p^3 v^3 m^2}{N^2 e^4} \right) \Delta\nu \\ &= \frac{16\pi^4 N^4 e^{10}}{c^3 m h^3 p^2 v^2 n^3} P \left(2\pi\nu \frac{p^3 v^3 m^2}{N^2 e^4} \right), \quad \dots \quad (54) \end{aligned}$$

where we have assumed that P is sufficiently constant in the frequency interval $\Delta\nu$.

Assuming that, instead of (22), the condition (38) is fulfilled, (54) must be replaced by

$$q_n h\nu = \frac{8\pi^4 N^4 e^{10}}{3c^3 m h^3 p^2 v^2 n^3} P' \left(2\pi\nu \frac{p}{v} \right). \quad \dots \quad (55)$$

Fig. 5.

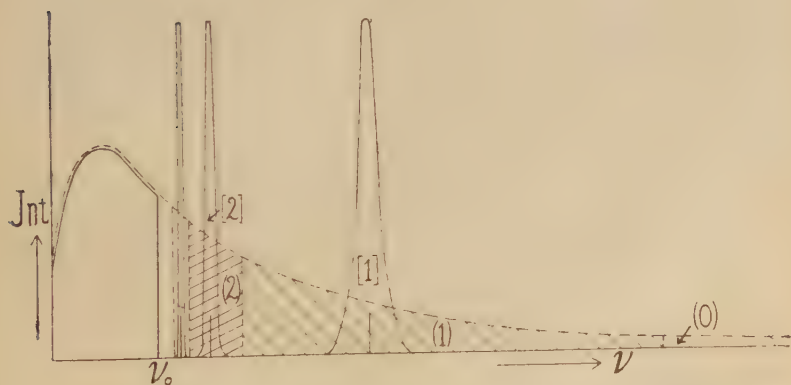


Fig. 5 illustrates the procedure followed. The dotted curve represents the energy distribution in the classical radiation; the full curves represent this distribution in the quantum problem. For frequencies smaller than the limit ν_0 , the two curves coincide. The frequency intervals which are assumed to correspond to the lines are separated by vertical dotted lines. According to our assumptions expressed in (54), the areas (1), (2), ... are equal to the areas [1], [2], ... That there will always be a large

frequency region extending to infinity in the classical energy distribution, which does not correspond to any transition, is a feature which has its analogy in the theory of simple and multiple periodic systems, where every possible radiation transition corresponds to an harmonic component in the motion, but not every harmonic component to a possible transition. Further, it needs hardly to be emphasized that there is a good deal of ambiguity in the choice for $\Delta\nu$ expressed by (53), especially as regards the binding in the one-quantum state. This point will be of special interest in the discussion of the results. Another interesting point to which we should like to draw attention is the difference between the classical ideas and the quantum theory assumptions which comes to light in the problem treated here. In fact, while on the classical theory the result of the collision of an electron with a nucleus, which is characterized by given values of r , p , and N , is uniquely determined, such a collision may on the quantum theory give rise to different results, the occurrence of which is governed by the laws of probability. Thus, after the collision the electron may either leave the nucleus with any velocity smaller than its original velocity or be bound by the nucleus in an n -quantum orbit. There will finally also be a finite probability for the electron not to radiate any energy at all. In our method of estimating the probabilities, this probability is clearly seen to be equal to the ratio of the part of the area of the dotted curve in fig. 5 designated by (0) to the total area of this curve. The probability that there occurs no radiation at all is therefore seen to become especially large for those values of the original angular momentum mpr of the electron for which the value of γ given by (33) becomes especially small*.

§ 5. *The atomic absorption coefficient for homogeneous X-rays.*

The formulæ of the former paragraph can be used for an approximate calculation of the efficient cross-section β , defined in § 2, which may be ascribed to a nucleus of charge Ne as regards its property of binding a free electron

* In order to explain that in some cases moving electrons apparently may pass through an atom without being influenced by it at all, Franck has enunciated the hypothesis that electrons which at a collision do not radiate should not be deflected from their original path. The consequences of this hypothesis have been investigated by F. Hund, *Zeitschr. f. Phys.* xiii. p. 241 (1923).

in an n -quantum orbit. In fact, constructing a plane passing through the nucleus which is perpendicular to the direction of the free electron before the collision, every surface element $d\sigma$ of this plane may be considered as contributing to the value of β with an amount equal to $q_n d\sigma$, where q_n is the quantity in formula (54) which depends on the distance ρ of the element $d\sigma$ from the nucleus, and which determines the probability that a free electron the original path of which cuts $d\sigma$ is captured in an n -quantum orbit. The total effective cross-section β may then be obtained by integrating $q_n d\sigma$ over the whole plane. We thus obtain, making use of (54), (33), and (32),

$$\begin{aligned}\beta &= \int q_n d\sigma = 2\pi \int_0^\infty q_n \rho d\rho \\ &= \int_0^\infty \frac{32\pi^5 N^4 e^{10}}{c^3 m h^4 p v^2 n^3 v} P\left(2\pi v \frac{p^3 v^3 m^2}{N^2 e^4}\right) d\rho \\ &= \frac{32\pi^5 N^4 e^{10}}{3c^3 m h^4 v^2 n^3 v} \int_0^\infty \frac{P(\gamma)}{\gamma} d\gamma = \frac{128\pi^4 N^4 e^{10}}{3\sqrt{3} c^3 m h^4 v^2 n^3 v} \cdot \cdot \cdot \quad (56)\end{aligned}$$

It is of interest to mention that we obtain the same formula if we take into account the fact that the frequency interval (53) is finite, instead of assuming, as was done in (54), that it can be considered as very small.

In (56) we have integrated over all values of ρ , and of γ , from 0 to ∞ , although formula (54) which has been used only holds in a certain limited region of ρ values. Thus (54) holds only as long as ρ is so small that $m\rho v^2/Ne^2$ is small compared with unity, corresponding, on the classical theory, to a nearly parabolic orbit of the electron. On the other hand, for values of ρ for which this expression is large compared with 1, the classical orbit of the electron will be nearly rectilinear, and formula (55), instead of (54), could have been applied in the calculation of $q_n \rho d\rho$. As a sufficient approximation we will therefore use the following procedure. We shall consider a value ρ_0 of ρ which makes $m\rho v^2/Ne^2$ just equal to 1, and which is therefore given by

$$\rho_0 = \frac{Ne^2}{mv^2} \cdot \cdot \cdot \cdot \cdot \cdot \quad (57)$$

For this value the classical orbit of the electron will be an equilateral hyperbola: for $\rho_0 < 1$ the angle between the asymptotes is less than $\pi/2$, for $\rho_0 > 1$ it will be larger

than $\pi/2$. Further, we will divide the integral $\int_0^\infty q_n p dp$ in two parts, $\int_0^{\gamma_0} q_n p dp$ and $\int_{\gamma_0}^\infty q_n p dp$, and apply (54) in the calculation of the former integral and (55) in the calculation of the latter. Introduced in (33), the expression (57) for μ corresponds to a value of γ given by

$$\gamma_0 = \frac{2\pi\nu N e^2}{m v^3}, \quad . \quad . \quad . \quad . \quad . \quad (58)$$

while, introduced in (45), it corresponds to exactly the same value for γ . Proceeding in this way, and introducing (55) in the integral $\int_{\gamma_0}^\infty q_n p dp$, we see that (56) must be replaced by

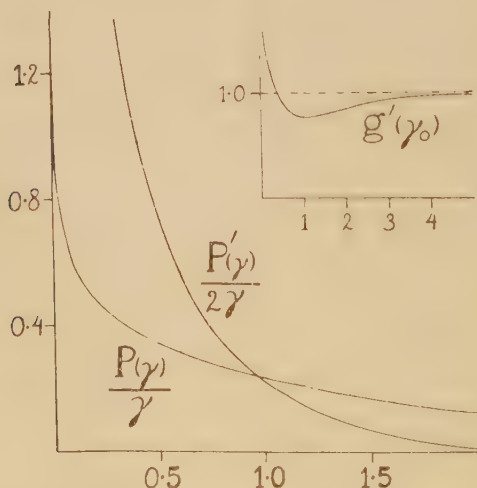
$$\beta = \frac{32\pi^5 N^4 e^{10}}{3c^3 m h^4 v^2 n^3 \nu} \left[\int_0^{\gamma_0} \frac{P(\gamma)}{\gamma} d\gamma + \int_{\gamma_0}^\infty \frac{P'(\gamma)}{2\gamma} d\gamma \right]. \quad (59)$$

Comparing with (56), this formula may be written in the form

$$\beta = \frac{128\pi^4 N^4 e^{10}}{3\sqrt{3} c^3 m h^4 v^2 n^3 \nu} g'(\gamma_0), \quad . \quad . \quad . \quad (60)$$

where g' is a numerical factor, depending on γ_0 , which is equal to the ratio of the sum of the two integrals appearing in (59) to the value which this sum assumes for $\gamma_0 = \infty$.

Fig. 6.



In order better to survey this result, we have in fig. 6 drawn curves representing $P(\gamma)/\gamma$ as well as $P'(\gamma)/2\gamma$ as

functions of γ . In the corner a graph of the function $g'(\gamma_0)$ is represented, which can be expressed as a finite sum of squares and products of Hankel functions. For γ_0 equal to zero, g' becomes infinitely large, due to the fact that the integral $\int_{\gamma_0}^{\infty} P'(\gamma) d\gamma/2\gamma$ diverges when γ_0 vanishes. In fact, for small γ_0 this integral is equal to $0.047 - 0.40 \log \gamma_0$. We see that for $\gamma_0 > 0.2$ the value of g' differs never more than 20 per cent. from unity, while for smaller values of γ_0 it may become considerably larger. γ_0 can also be written in the following form:

$$\gamma_0 = \frac{1}{2} \frac{\nu}{\nu_0} \sqrt{\frac{\nu_K}{\nu_0}}, \quad (61)$$

where ν_0 is the frequency "corresponding" to an energy quantum $\frac{1}{2}mv^2$, according to the formula

$$h\nu_0 = \frac{1}{2}mv^2, \quad (62)$$

while ν_K is the frequency corresponding to the energy with which the electron is bound in a 1-quantum orbit,

$$\nu_K = \frac{2\pi^2 N^2 e^4 m}{h^3}. \quad (63)$$

This frequency coincides closely with the frequency of the K-absorption limit. The frequency ν entering in the expression for β is (*cf.* (11)) obviously connected with ν_0 and ν_K by the relation

$$\nu = \nu_0 + \frac{\nu_K}{n^3}. \quad (64)$$

Before proceeding, we must still consider two errors involved in the deduction of (60), referring to the conditions (b) and (c) on p. 848 and p. 851. In fact, for given N and r our formula (54) for q_n obtained from the consideration of a parabolic orbit loses its validity for small values of p , since the radiation in the classical orbit will no longer be small (condition (34)), and since the velocity of the electron no longer remains small compared with the velocity of light (condition (35)). In consequence of this there will be a region of p values, extending from zero, for which the value of the integrand in (59) may involve a considerable error. Elimination of p between (33) and the second of the formulæ (36) shows, however, that in the region of ν and N values covered by the experiment ($\lambda > 0.1 \text{ \AA}$, $N < 93$) the error due to the first of the causes mentioned above may be neglected except for small values of ν , *i. e.* for small values of the ratio ν_0/ν . On the

other hand, the influence of the second cause (large velocity of the electron) may for large N and especially for large v and ν have some effect on the final result.

Attention must further be drawn to a possible source of error of another kind. We must expect that, by the emission of radiation, the angular momentum of the electron round the nucleus cannot change by more than $h/2\pi$ *. Now the possible values of the angular momentum of an electron bound in an n -quantum orbit are equal to $1, 2, 3, \dots, n$. It would therefore seem reasonable to extend the integral (56) in (59) not to ∞ but to an upper limit p_1 corresponding to an angular momentum mpr equal to $(n+1)h/2\pi$. It can, however, readily be shown that this would influence the final result very little. In fact the upper limit p_1 for p , to be introduced in the integration (59), is found by introducing $p_1 = (n+1)h/2\pi mvr$ in (33) or in (45) according as $p_1 < p_0$ or $p_1 > p_0$ (cf. p. 857), or, what is the same, according as $\nu_0/\nu_K < 1/(n+1)^2$ or $\nu_0/\nu_K > 1/(n+1)^2$. Restricting ourselves here to the latter case, the upper limit γ_1 in the integral $\int_{\gamma_0}^{\gamma_1} P'(\gamma) d\gamma/2\gamma$ is easily seen to be equal to $\frac{\nu}{\nu_0} \frac{n+1}{2}$, and therefore always larger than $(n+1)/2$. From the curve for $P'(\gamma)/2\gamma$ it is seen that the introduction of this upper limit instead of ∞ will never influence the value of β materially.

It is seen that the errors which are introduced on account of the conditions (22) or (38) and (35) not being fulfilled are only due to the introduction of purely mathematical simplifications, and therefore might be discarded by a more elaborate analytical treatment in which the orbits are no longer considered as either parabolic or rectilinear, and in which relativity dynamics are used throughout †. On

* N. Bohr, 'On the Quantum Theory of Line Spectra,' Copenhagen Academy, 1918, Part I, p. 34; A. Rubinowicz, *Physikal. Zeitschr.* xix. pp. 441, 465 (1918).

† Note added during the proof. If the calculations are carried through, without the introduction of any restrictions regarding the value of the ϕ_0 in (18), we meet with Hankel functions the order of which is expressed by a complex number. The final result for the value of β is found to be of the form (60), where

$$g'(\gamma_0) = \frac{\pi\sqrt{3}}{4} i\gamma_0 H_{i\gamma_0}^{(1)}(i\gamma_0) H_{i\gamma_0}^{(1)}(i\gamma_0). \quad \left(H_p^{(1)}(x) = \frac{dH_p^{(1)}(x)}{dx} \right).$$

The graph of $g'(\gamma_0)$ given in figure 6 agrees rather closely with this expression. For large values of γ_0 it can asymptotically be represented by $1 - 0.218 \gamma_0^{-2/3}$, while for small values of γ_0 it becomes equal to $-\frac{\sqrt{3}}{\pi} (1 + \pi\gamma_0) \log \frac{\gamma_0}{2}$ if terms containing second and higher powers of γ_0 are omitted.

the other hand the errors in the region of small values of ν_0/ν , which will be due to the conditions (34) or (46) not being fulfilled, are inherent in the method.

After these digressions referring to the limits of the validity of our formulæ, we will now proceed to determine the atomic absorption coefficient α_τ for X-rays referring to an atom consisting of a nucleus which has bound one electron in an n -quantum orbit. This coefficient, according to our considerations in § 2, will be closely connected with the probability that a nucleus captures a free electron and binds it in such an orbit. From (17) and (60) we have thus :

$$\alpha_\tau = \frac{m^2 r^2 c^2}{2 a h^2 \nu^2} \beta = \frac{64 \pi^4 N^4 e^{10} m}{3 \sqrt{3} a_n c h^6 n^3 \nu^3} g' = \frac{64 \pi^4 e^{10} m}{3 \sqrt{3} c^4 h^6} g' \frac{N^4 \lambda^3}{a_n n^3} \\ = 0.0104 \cdot g' \frac{N^4 \lambda^3}{a_n n^3}, \quad (65)$$

where we have introduced the wave-length λ (measured in cm.), and where a_n , the statistical weight of the atom in its n -quantum state, is equal to $n(n+1)$.

Formula (65) may be used to find an expression for the effective absorbing cross-section of *neutral atoms* for homogeneous X-rays. In fact, we may assume that the probability for the expulsion of a K, L, or M electron from the interior of a neutral atom by means of X-rays in first approximation will be the same as the probability of expelling from an atom containing only one electron an electron from a 1-, 2-, or 3-quantum orbit. Denoting by b_n the number of electrons present in n -quantum orbits, we get thus the following expression for the atomic (true) absorption coefficient for an element of atomic number N :

$$\alpha_\tau = g \cdot 0.0104 N^4 \lambda^3, \quad (66)$$

$$g = g' \left(\frac{b_1}{a_1} + \frac{b_2}{8a_2} + \frac{b_3}{27a_3} + \dots \right), \quad (67)$$

where the first term in the brackets corresponds to the K-group, the second to the L-group, etc. This formula should of course hold only for wave-lengths shorter than the K-limit L_K ; for wave-lengths longer than L_K but shorter than L_L , the first term in the expression for g should be omitted; for wave-lengths longer than L_L but shorter than L_M , the two first terms should be omitted; etc.

As regards the application of formula (67), several points are to be observed. First of all we meet the question

whether it is justifiable to consider the different electrons in the same group as independent of each other, and to ascribe a statistical weight $n(n+1)h^3$ to each of them, disregarding the division of the groups into sub-groups. In order to investigate this problem, let us consider the case of an atom containing one electron which is exposed to an external field of force, *e. g.* a homogeneous magnetic field. Taking, moreover, the relativity modifications in the laws of mechanics into account, the orbit of the electron in the stationary state will be described, besides by the principal quantum number n , by two auxiliary quantum numbers, in such a way that each stationary state corresponding to a given value of n appears split up into $n(n+1)$ states corresponding to slightly different values of the energy, and each possessing a statistical weight h^3 . Considering one of these states, we may again define an efficient cross-section β governing the probability that a free electron colliding with the nucleus is bound in this state with the emission of radiation, and an efficient cross-section α governing the probability that the electron in this state is expelled from the atom due to incident monochromatic radiation. The relation between α and β will be given by (17) if a in this formula is put equal to 1 instead of $n(n+1)$. On the other hand, if we apply our method of estimating the value of β we are led to an expression for this quantity which is $n(n+1)$ times smaller than that given by (60). In fact, the frequency-interval which was defined by (53) corresponds to a binding of the electron in *any* n -quantum orbit, and must therefore in the present case be divided by the number indicating in how many states of equal weight the n -quantum state is split up. This may be illustrated by observing that when the n -quantum state is split up in different sub-states under the influence of the external field, the tendency for the colliding electron to be bound in this or in that sub-state will depend on the orientation of its original path with respect to the nucleus and the direction of the field. From these considerations it is seen that the value of α will always be the same as that given by (65), whether regard is taken of the sub-states or not.

The assumption that in the problem of the removal of an electron from a completed group in the *neutral* atom the same formula (65) may still be applied to each electron in the group, and with the same value of a_n , is made highly probable by arguments of similar nature. Thus, considering for instance the K-group, the ratio between the statical

weight of the atom in its neutral state and in an ionized state in which one electron is removed is no longer $2h^3$, but less than that (probably $\frac{1}{2}h^3$ *). On the other hand, a free electron colliding with the ionized atom will by no means have the same chance of being captured in a 1-quantum orbit as in the case of a collision with a free nucleus. In fact, such a capturing process can only take place for especially favourable orientations of the original path of the colliding electron with respect to the orbit of the K-electron already present in the atom, and it is reasonable to expect that this effect will just cancel out the other effect which was due to the statistical weight.

As well known, the L, M, ... absorption limits consist actually each of several limits lying close to each other; this fine-structure is intimately connected with the division of the electron groups in the atom into sub-groups; but certain difficulties are still involved in its detailed interpretation†. The determination of the contributions of the different L-limits, M-limits, etc. to the total L-absorption, M-absorption, etc. lies outside the scope of our present considerations.

Another point which needs consideration when formula (67) is applied, is that the different terms on the right side of (67) can only be expected to hold if the corresponding group of electrons is well in the interior of the atom, so that the energy with which these electrons are bound differs only little from the binding of an electron in an orbit of the same quantum number by a free nucleus. If the sum in (67) is also extended to the outer groups of the atom, the terms corresponding to these groups will be very inaccurate and probably too large. We may expect that here also errors in our expressions for β will come in, which are due to the fact that in § 3, instead of considering the binding of an electron by an atom which has lost one electron, we considered the binding by an atom which has lost all its electrons. On the total amount of absorption these errors have, however, little influence, at any rate for small wave-lengths, since the absorption due to the inner groups is much larger than that due to the outer groups.

Introducing in (67) the values $b_1=2$, $b_2=8$, $b_3=18$, which according to Bohr's theory are the number of electrons present in the K, L, and M groups, for all elements for which $N \gg 29$, we get

$$g = g'(1 + \frac{1}{6} + \frac{1}{18} + \dots). \quad (68)$$

* Cf. N. Bohr, *Ann. der Physik*, lxxi. p. 271 (1923).

† Cf. N. Bohr and D. Coster, *Zeitschr. für Physik*, xii. p. 342 (1923).

The first term, which is due to the absorption of the K electrons, is seen to be preponderant over the following terms. This is in agreement with the experiments, which have shown that there is a very great difference in the absorption coefficient on both sides of the K-limit. While for the elements from molybdenum (42) to tin (50) the ratio between the α -values on the short and long wave-length side of this limit amounts to about 6:1*, there are also values in the literature for such a heavy element as lead ($N=82$) (3.5:1)†, and such a light element as aluminium ($N=13$) (11:1)‡; but the two latter ratios, which are each only based on a single observation, are extremely uncertain. On our formula we should expect a ratio of about 5.5:1 for heavy elements, while for light elements, due to the errors just mentioned, this ratio might be expected to be somewhat larger. The agreement must be considered satisfactory, especially if we remember how large an ambiguity there is involved in our fixation of the $\Delta\nu$ -value for a one-quantum orbit in (53), as a consequence of which there is a rather big uncertainty in the ratio between the first two terms in (68).

If we bear in mind the approximative character of the whole method of estimating probabilities, and remember that the factor g in general does not differ much from unity (*cf.* p. 859), we arrive at the conclusion that for wave-lengths shorter than the K-limit the expression (66) may be expected to hold with a value for g which has the same order of magnitude as unity. The agreement with the empirical formula (5) is very satisfactory, especially if we remember that the measured absorption coefficients cover a region in which the lowest values are several hundred times smaller than the biggest values. The observed value for C (0.0229 [Richtmeyer] or 0.0244 [Wingårdh]) corresponds to a value for g equal to 2.2 or 2.4.

Many authors have found that for a given element or for a given wave-length the observations are better described by an exponent of λ somewhat less than 3, or an exponent of N somewhat less than 4§, proving that

* Glocker, *Physikal. Zeitschr.* xix. p. 71 (1918); F. K. Richtmeyer, *Phys. Rev.* xviii. p. 13 (1921); K. A. Wingårdh, Dissertation, Lund, 1923. The values given in literature vary between 5.5 and 7: compare Williams and Worsnop, *Nature*, cviii. p. 306 (1921).

† Hull and Rice, *Phys. Rev.* viii. p. 326 (1916); comp. also Williams and Worsnop, *loc. cit.*

‡ C. D. Miller, *Phys. Rev.* viii. p. 329 (1916).

§ Compare the papers cited on p. 837.

formula (5) only can be considered as a first approximation. Richtmeyer remarks especially that for wavelengths not much shorter than the K-limit, his formula gives values which are too high. This may be due to the mathematical simplifications introduced in our calculations, and may also be connected with the circumstance that just in this region the theory on which our formulæ are based may be expected to fail in principle (compare p. 860).

§ 6. *The Energy Distribution in the continuous X-ray Spectrum.*

Formulæ (50) and (51) in § 4 give expressions for the energy distribution in the radiation which will ensue from the collision of a great number of electrons possessing the velocity v with nuclei of charge Ne , if the distance from the nucleus to the original path of the colliding electron is equal to ρ . As explained on p. 852, these formulæ may be expected to hold approximately for frequencies smaller than the limit ν_0 given by (62); for larger frequencies the spectrum will consist of a series of discrete lines. To a first approximation we may assume that also the spectrum excited by swift electrons colliding with *neutral* atoms may be calculated in the same way, with the difference of course that no frequencies will be emitted larger than the limit ν_0 . This assumption finds a justification, discussed below in more detail, that, as a consequence of it, most of the radiation is contributed by electrons penetrating right into the interior of the atom, where the influence of the other electrons compared with that of the nucleus is very small.

We shall first consider the radiation which would be emitted in one second from a surface element $d\sigma$ of an infinitely thin target containing A atoms of atomic number N per cm.^2 , which is bombarded by a beam of cathode rays of velocity v in which s electrons in one second pass across a cross-section of 1 cm.^2 . The energy $i_\nu d\sigma d\nu$ in this radiation which lies between frequencies ν and $\nu + d\nu$ will obviously be given by an integral:

$$i_\nu d\sigma d\nu = s \cdot A d\sigma d\nu \int_0^\infty 2\pi p q(\nu) h\nu dp, \quad . \quad . \quad (69)$$

where $q(\nu)h\nu$ is given by the expressions (50) or (51). Introducing the expression (50), *i.e.* assuming that the

condition (22) is fulfilled with sufficient approximation, we get

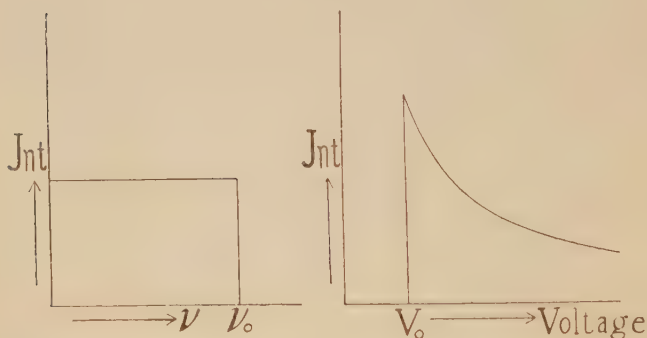
$$i_\nu d\sigma d\nu = sA d\sigma d\nu \int_0^\infty \frac{8\pi^3 N^2 \rho^6}{c^3 m^2 p^2} P\left(2\pi\nu \frac{p^3 v^3 m^2}{2N^2 e^4}\right) dp. \quad (70)$$

Introducing the quantity γ , given by (33), as integration variable, we get

$$\begin{aligned} i_\nu d\sigma d\nu &= sA d\sigma d\nu \frac{8\pi^3 N^2 \rho^6}{3c^3 m^2 v^2} \int_0^\infty \frac{P(\gamma)}{\gamma} d\gamma \\ &= \frac{32\pi^2}{3\sqrt{3}} \frac{N^2 e^6}{c^3 m^2 v^2} s \cdot A d\sigma d\nu. \quad \dots \quad (71) \end{aligned}$$

This expression does not contain ν , so that i_ν has a constant value for frequencies between zero and the Duane-Hunt limit ν_0 , while it is zero for $\nu > \nu_0$. A graphical representation is given on the left side of fig. 7. On the right

Fig. 7.



side the form of the theoretical "isochromate" in the spectrum of the infinitely thin target is given, which gives the dependency of the energy of a given small frequency interval on the voltage applied. Since the voltage is proportional to the square of the velocity, the isochromate will have the form of a piece of an hyperbola which starts from the minimum voltage V_0 at which the radiation of the frequency considered can be excited*.

In the deduction of (71) it was assumed that in the integral (69) the classical orbit of the electron could, with

* Compare D. L. Webster and A. E. Hennings, Phys. Rev. xxi. p. 312 (1923), where the corresponding curves for an infinitely thin target are drawn, derived by means of the Thomson-Whiddington law from the experiments.

sufficient approximation, be considered as parabolic (condition (22)). For increasing values of p , however, the orbit will become hyperbolic and finally become nearly rectilinear. We shall apply the same procedure as that applied in the former paragraph, *i. e.* we shall divide the integral (69) in two parts—one extended over p values for which the angle between the asymptotes is less than 90° , using the expression (50) for $q(\nu)$, and one extended over p values for which this angle is larger than 90° and in which the expression (51) for $q(\nu)$ is used. This means that the integral in (71) must be replaced by the sum of the two integrals appearing in (59), where γ_0 is again defined by (58) or (61). Introducing, just as on p. 858, the quantity g' , the only change which must be made in formula (71) consists in the addition of the factor g' . Since the latter quantity varies only slightly with varying γ_0 , *i. e.* with varying ν , ν_0 , and N , this addition does not affect the results materially, and in the following formulæ the factor g' will be omitted.

An easy calculation shows that the integrand in (69) takes its maximum value for p equal to about $p_K \sqrt{\frac{\nu_K}{\nu_0}} \sqrt[3]{\frac{2\nu_K}{\nu}}$, where p_K denotes the radius of the orbit of a K electron, while for p twice as large the relative magnitude of the integrand has become very small. This shows that the observed radiation is mainly due to electrons which penetrate right into the interior of the atom. In fact, choosing a very unfavourable case—*i. e.* a heavy element (Pt) and a low voltage (7000 volt, $\lambda_0 = c/\nu_0 = 1.18$ Å.), and a rather long wavelength ($\lambda = c/\nu = 1.7$ Å.),—we find that the maximum in question lies at about $p = 11 p_K$. This distance corresponds to the region of the M electrons where the screening action of the inner electrons on the colliding electron is still small.

In the experiments on the continuous X-ray spectrum we have to do with a target of finite thickness in which the cathode rays penetrate, losing kinetic energy on their way through the atoms. The loss of energy will be due to the emission of X-rays only to a very small extent; its main cause is the expulsion of electrons from the interior of the atom, which will give rise to the emission of characteristic X-ray radiation. The latter problem has recently been theoretically investigated in detail by Rosseland*, who was able to account for the laws holding for the dependency of

* S. Rosseland, Phil. Mag. xlv. p. 65 (1923).

the intensity of the characteristic X-rays on the voltage applied. Rosseland's considerations are based on Bohr's theory for the stopping of swiftly-moving electrified particles through matter*, which gives a rational theoretical explanation of the well-known Thomson-Whiddington law. This law states that the decrease of the velocity of an electrical particle in matter is governed by the formula

$$\frac{dr^4}{dx} = -a, \quad . \quad . \quad . \quad . \quad . \quad . \quad (72)$$

where dx is an element of the path of the particle, while a is a constant characteristic for the substance. Bohr gives a theoretical formula for a which in the case of β rays and cathode rays assumes the form :

$$a = \frac{16\pi e^4 A}{m^2} \sum_i \log \left(\frac{kv^3 m}{4\pi v_i e^2} \right). \quad . \quad . \quad . \quad (73)$$

Here A denotes the number of atoms in unit volume, while k is a numerical constant equal to 1.1. The summation has to be extended over all electrons in the atom; v_i is a quantity of the same order of magnitude as the frequency of revolution of the electron round the nucleus. Assuming a kind of mean value \bar{v}_i of the v_i -values of the different electrons, (73) may be written :

$$a = \frac{16\pi e^4 A N l}{m^2} = 1.957 \cdot 10^{42} \frac{A}{M} N l, \quad . \quad . \quad . \quad (74)$$

where N is the atomic number and M Avogadro's number, while l has the dimensions of a number and is equal to $\log(kv^3 m / 4\pi \bar{v}_i e^2)$. Due to the logarithm, l depends only slightly on v , nor is it very sensitive to our assumptions on the value of v_i . Thus for a value of v corresponding to 10,000 volts, and taking $\bar{v}_i = 10^{17}$, we get $l = 6.6$. When the velocity has decreased to 5000 volts, l decreases by about 1, while the assumption that \bar{v}_i is 2.72 times larger causes also a decrease of l by 1. Thomson-Whiddington's law agrees very well with the experiments†. As regards the value of a , the recent experiments by Terrill‡ on Be, Al, Ca, Ag, and Au are in very good agreement with Bohr's theory. Thus the empirical values of l for these elements are equal to 5.9, 5.5, 5.5, 5.8, and 7.3.

* N. Bohr, Phil. Mag. xxv. p. 10 (1913) and xxx. p. 381 (1915).

† R. Whiddington, Proc. Roy. Soc. lxxxvi. p. 360 (1912).

‡ H. M. Terrill, Phys. Rev. xxi. p. 476 (1923). The recent experiments of B. F. J. Schonland (Proc. Roy. Soc. civ. p. 235 (1923)) on the range of cathode rays in Al, Cu, Ag, and Au foils give also a very close confirmation of Bohr's theory.

Returning now to the continuous X-ray spectrum, the spectrum emitted from a finite target will be obtained by summing the radiations which will be emitted by the electrons at the various stages of their velocity in the target. Denoting the energy between ν and $\nu + d\nu$ in the total radiation per second by $I_\nu d\sigma d\nu$, the quantity I_ν can obviously be derived from the intensity function (71) for an infinitely thin target by means of the integral

$$I_\nu = \int_{v_0}^{v_\nu} i_\nu \frac{dx}{dv} dv = - \int_{v_0}^{v_\nu} i_\nu \frac{4v^3}{a} dv, \quad . \quad . \quad . \quad (75)$$

where v_0 is the original velocity of the electrons, while v_ν means the velocity for which $h\nu = \frac{1}{2}mv_\nu^2$. Introducing the expression (71) for i_ν , and the expression (74) for a , we have

$$\begin{aligned} I_\nu &= - \int_{v_0}^{v_\nu} \frac{32\pi^2 N^2 e^6}{3\sqrt{3}c^3 m^2 v^2} \cdot s \cdot A \cdot \frac{4v^3 m^2}{16\pi e^4 ANl} dv \\ &= -s \int_{v_0}^{v_\nu} \frac{8\pi}{3\sqrt{3}l} \frac{e^2}{c^3} N v dv = s \cdot \frac{4\pi}{3\sqrt{3}l} \frac{e^2}{c^3} N (v_0^2 - v_\nu^2). \end{aligned}$$

Introducing instead of v_0 and v_ν the frequency ν_0 of the Duane-Hunt limit ($\frac{1}{2}mv_0^2 = h\nu_0$) and the frequency ν we get, putting $l=6$,

$$I_\nu = s \cdot \frac{8\pi}{3\sqrt{3}l} \frac{e^2 h}{c^3 m} N (\nu_0 - \nu) = s \cdot 4.95 \cdot 10^{-50} N (\nu_0 - \nu), \quad . \quad . \quad . \quad (76)$$

which is identical with formula (1C), given in the first paragraph, and is in general agreement with the experiments.

In the foregoing calculation two factors have been neglected. Firstly the absorption of rays in the target, which originate from atoms in the interior of the target. K\u00fchlenkampff as well as Webster have, however, made corrections for this absorption*. Secondly, the electrons will not only lose kinetic energy at their collisions with the atoms but they will also be deflected through large angles, so that in general they will penetrate much less deeply into the target than when their path was straight†. Due to these deflexions, a fraction of the electrons will be able to leave the target ("reflexion" of cathode rays‡), some of them with very small velocities, but many of them

* D. L. Webster and A. E. Hennings, *Phys. Rev.* xxi, p. 301 (1923).

† Compare D. L. Webster and A. E. Hennings, *loc. cit.*

‡ Cf. A. Becker, *Ann. d. Phys.* xvii, pp. 387, 447 (1905); A. Kovarik, *Phil. Mag.* xx, pp. 849, 866 (1910); B. F. J. Schonland, *loc. cit.* p. 240.

also with velocities about equal to the initial velocity v_0 . The latter effect increases considerably with the atomic number, and will materially contribute to the appearance of the "bend" in Kuhlenskampf's curves, for which the second term on the right hand of (7) gives an approximate expression.

The problem of the differences in the intensity distributions in the radiations which are observed at different angles with the direction of the cathode rays*, claims obviously a closer examination of these deflexions in the target. In fact, the spectrum due to an infinitely thin target will, as seen from the difference in the curves $\phi(\gamma)$ and $\psi(\gamma)$, or $\phi'(\gamma)$ and $\psi'(\gamma)$, (compare figs. 1 and 3), in general be different when observed in different directions. For targets of finite thickness this effect will no longer appear in the radiation due to electrons which have lost a part of their original velocity, since, due to the deflexions, the directions of the motions of these will be distributed almost at random.

We will not enter here on this problem, nor will we discuss the difficult question (mentioned on p. 838) of the asymmetry of the radiation with respect to a plane perpendicular to the cathode rays†. We shall here only draw attention to an important question which we meet with when considering more closely the assumptions underlying our calculations. Thus we have, as stated in the beginning of § 4, assumed that any radiation takes place by the emission of monochromatic quanta $h\nu$. This assumption, which is so essential in the applications of the quantum theory to line spectra, can no doubt also be applied to a process where a free electron is bound by an atom with emission of radiation. This seems to follow directly from photoelectric phenomena, especially from M. de Broglie's beautiful experiments‡. In the case of a free electron which loses so little energy by a collision that it leaves the atom again with a finite velocity, the assumption in question cannot be tested directly however, and the time which the collision takes is so short—presumably much shorter than the time which the emission of a monochromatic quantum $h\nu$ necessarily must take—that it at first sight would seem uncertain whether Bohr's frequency relation can be applied also here. Notwithstanding these difficulties there seems on the other hand to be no reason

* Compare Wagner, *Phys. Zeitschr.* xxi. p. 621 (1920).

† See N. Bohr, *Zeitschr. f. Phys.* xiii. p. 154 (1923).

‡ See, for instance, the Report of the Solvay Conference held at Brussels in 1921.

to be afraid that the estimation in § 4 of the intensity distribution in the continuous spectrum, which forms the basis of the calculations in this paragraph, should be less valid. In fact, the success of the applications of the correspondence principle makes it extremely probable that a comparison with the radiation which would be emitted on the classical theory will always afford a method of determining approximately the energy distribution in the actual radiation.

Finally we will apply the formulæ of this paragraph to the calculation of the total amount of radiation. From (76) we find that the radiation energy which in the mean will be due to the impact of a single electron on the target, is equal to

$$I = \frac{8\pi}{3\sqrt{3}l} \frac{e^2 h}{c^3 m} \int_0^{v_0} N(v_0 - v) dv = \frac{4\pi}{3\sqrt{3}l} \frac{e^2 h}{c^3 m} N v_0^2 \\ = \frac{\pi}{3\sqrt{3}l} \cdot \frac{e^2 m}{c^3 h} N v^4. \quad (77)$$

The ratio to the kinetic energy $\frac{1}{2}mv^2$ of the electron will give the efficiency coefficient of the X-ray tube:

$$\text{Eff.} = \frac{2\pi}{3\sqrt{3}l} \frac{e^2}{ch} N \left(\frac{v}{c}\right)^2 = 2.34 \cdot 10^{-4} N \left(\frac{v}{c}\right)^2. \quad (78)$$

The efficiency of X-ray production has been investigated by many physicists*. Beatty† has deduced from his experiments the following approximate formula for the efficiency:

$$\text{Eff.} = 2.54 \cdot 10^{-4} B \left(\frac{v}{c}\right)^2, \quad . \quad . \quad . \quad (79)$$

where B is the atomic weight, which is about equal to 2N. The agreement must be considered satisfactory, if we remember that in the deduction of (78) a large number of factors are neglected. For the first, we have disregarded the absorption in the target itself and in the walls of the tube, by which a good deal of energy is lost, especially in the region corresponding to small frequencies. Secondly, we have disregarded the characteristic radiation, which is quite of the same order of magnitude as the continuous radiation, and the intensity of which is also roughly proportional to the fourth power of the velocity of the cathode rays‡.

* Compare the survey given by Bergen Davis, Bulletin of the National Research Council, vol. i. Part 7 (Dec. 1920).

† R. T. Beatty, Proc. Roy. Soc. lxxxix. p. 314 (1913).

‡ Compare S. Rosseland, Phil. Mag. xlv. p. 65 (1923).

XCIV. *Critical Electron Energies in Hydrogen.* By FRANK HORTON, *Sc.D., F.R.S.*, and ANN CATHERINE DAVIES, *D.Sc.**

IN the Proceedings of the Royal Society, A, vol. xcvii. p. 1 (1920) the authors have given an account of an investigation of critical electron energy values in hydrogen. The experiments described in this paper were carried out in order to ascertain whether the positive ions which could be detected leaving a positively charged platinum surface under electronic bombardment could be attributed to hydrogen occluded in the metal, but the results obtained afforded no support for such a view. From the experiments in hydrogen it was concluded that there are two critical electron energies at which radiation is produced, and two at which ionization occurs, and from the approximate agreement between the values obtained and the values predicted from Bohr's theory, the first radiation voltage and the first ionization voltage were attributed to the hydrogen atom, and the other two critical values to the hydrogen molecule. It was assumed that at the higher ionization voltage the molecules are dissociated into pairs of atoms and that one atom of each pair is ionized. As the experiments in hydrogen were performed mainly with a view to comparing the critical points obtained in the gas with the point at which a positive ion current commenced under the electronic bombardment of the platinum gauze in a high vacuum, the investigation was not extended to applied accelerating voltages greater than 20, and the determination of the absolute values of critical points was only approximate.

During the past year the authors have carried out a much fuller investigation of the effects of electron collisions with hydrogen, partly with a view to ascertaining the critical electron energy values more accurately than was possible with the apparatus used in the earlier research, but mainly in the hope of determining experimentally whether the radiation or ionization occurring at a critical stage is of atomic or of molecular origin. The method used for testing the origin of a radiation was to ascertain whether it could be absorbed and re-emitted by the gas in its normal state. This test was made by investigating whether the radiation in question would travel through the gas and produce a photo-electric effect on an electrode so placed that it could not be illuminated either directly, or by reflexion, from the position

* Communicated by the Authors.

at which the exciting electron collisions occurred. As hydrogen in the normal state is in the molecular condition, such a "handing-on" of radiation cannot occur if the radiation is produced by dissociation of the molecule into atoms and the excitation of one of these atoms, but only if the radiation is of true molecular origin. The test of the nature of the positive ions produced at a critical ionization stage was a spectroscopic examination of the radiation produced when recombination occurs, the assumption being made that the Balmer lines are due to the recombination of electrons and positive hydrogen atoms and that they therefore only appear if atoms are present.

Since the completion of our earlier research several investigations of the effects of electron bombardment of hydrogen have appeared*. Of these, the investigations by Duffendack and by Olmstead, which have been published while the present investigation was in progress, are particularly interesting in that they are attempts to distinguish the critical energy stages which are due to the molecule from those which are due to the atom. Olmstead's experiments enabled him to attribute certain energy stages definitely to collisions of electrons with molecules, but they did not provide any experimental basis for distinguishing between the molecular energy stages at which dissociation occurs and those at which no dissociation takes place. Duffendack's experiments, which were of a spectroscopic nature, led him to conclude that the ionization which is produced at 16 volts results from collisions of electrons and hydrogen molecules, at which dissociation of the molecule into atoms and the ionization of one of these atoms occurs. The reason for this conclusion was that when the arc in hydrogen was obtained at 16 volts, not only the secondary spectrum lines but also the Balmer series lines were present, indicating the presence of hydrogen atoms.

The present experiments have indicated that the following voltages correspond to critical electron energy values in hydrogen:—10.2 volts, 11.9 volts, 12.6 volts, 13.5 volts, 15.9 volts, 22.8 volts, 26.1 volts, and 29.4 volts. At the

* J. Franck, P. Knipping, and Thea Kruger, *Deutsch. Phys. Ges. Verh.* xxi. p. 728 (1919); C. Found, *Phys. Rev.* xvi. p. 41 (1920); F. L. Mohler and P. D. Foote, *Sci. Papers, Bur. of Stan.* 400, p. 669 (1920); F. L. Mohler, P. D. Foote, and E. H. Kurth, *Phys. Rev.* xix. p. 414 (1922); K. T. Compton and P. S. Olmstead, *Phys. Rev.* xvii. p. 45 (1921); P. E. Boucher, *Phys. Rev.* xix. p. 189 (1922); P. S. Olmstead, *Phys. Rev.* xx. p. 613 (1922); O. S. Duffendack, *Phys. Rev.* xx. p. 665 (1922).

critical values 10.2 volts, 11.9 volts, 12.6 volts, and 26.1 volts an increased rate of production of radiation commences, while at the values 13.5 volts, 15.9 volts, and 29.4 volts an increased rate of production of ionization commences. At 22.8 volts the bombarding electrons suffer inelastic collisions, but these are not accompanied by the production of more radiation or more ionization. The experiments indicate that 10.2 volts and 13.5 volts are atomic critical points, and that 11.9 volts, 12.6 volts, 15.9 volts, and 22.8 volts are molecular critical points. They show that the radiation produced at 11.9 volts can be "handed on" throughout a volume of the gas, and that it is therefore due to an excitation of a molecule without dissociation. They confirm Duffendack's observation that the Balmer series lines appear at the 16-volts ionization stage and show, therefore, that at this stage the dissociation of the molecule into atoms and the ionization of one of these atoms occurs.

A blue glow, whose spectrum was continuous and extended from the yellow to the limit of the visible spectrum in the violet, was obtained at lower voltages than either the Balmer lines or the lines of the hydrogen secondary spectrum, and without any ionization occurring. The experimental evidence suggests that this continuous spectrum is to be attributed to the formation of molecules (H_2 or possibly H_3) by the combination of neutral atoms produced by electronic-molecular encounters which result in dissociation and atomic excitation.

The results obtained are consistent with the view suggested by Pauli* from theoretical considerations, that the ionization of the hydrogen molecule by the process $H_2 \rightarrow H_2^+ + \text{electron}$ requires about 23 volts energy, whereas by the process $H_2 \rightarrow H + H' + \text{electron}$ it requires considerably less energy.

Description of Apparatus.

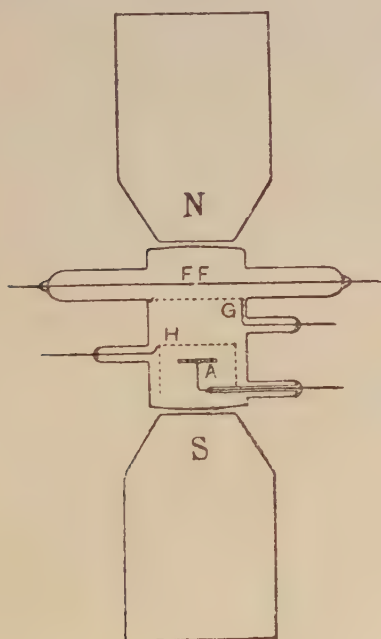
Three forms of apparatus were employed in the present series of experiments, two for the spectroscopic investigation, and one for the accurate location of the critical electron energy values and the investigation of the origin of the various radiations. The latter form of apparatus is identical with that employed by the authors in their experiments on the "handing-on" of radiation in helium, and is described in detail in a former paper†. Those employed

* W. Pauli, Jr., *Ann. der Phys.* lxviii. p. 177 (1922).

† *Phil. Mag.* xlii. p. 746 (1921).

for the spectroscopic investigation have also been used by the authors in previous researches* and will therefore be only briefly referred to here. Fig. 1, which is reproduced from the Proceedings of the Royal Society, A, vol. cii. (1922), indicates the arrangement of electrodes used in one of these forms. This apparatus was so constructed that it could be placed between the poles of a strong electromagnet whereby a concentration of the luminosity into a bright column parallel to the slit of the spectroscope could be effected.

Fig. 1.



The filaments F, F, only one of which was used at a time, were platinum strips coated with a mixture of lime and baryta, and the other electrodes were of platinum. The spectroscope was placed so as to view the part of the tube between G and H in the direction of the lengths of the filaments, the maximum intensity of luminosity being thus in line with a vertical plane through the axis of the collimator.

The other form of apparatus used for the spectroscopic

* Proc. Roy. Soc. A, c. p. 599 (1922), and cii. p. 131 (1922).

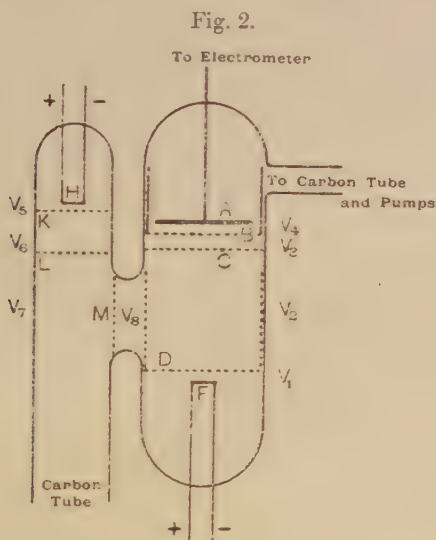
investigation was designed for the production of arcs at low voltages, and was a two-electrode tube with a filament of tungsten and a spherical platinum anode whose distance from the filament could be varied from 1 mm. to 20 mm.

Experiments with the form of apparatus represented in fig. 1 were carried out with two different arrangements of electric fields. In both cases the electrons from the hot filament were accelerated towards the gauze G by means of a difference of potential which could be altered in steps of one-tenth of a volt. A milliammeter (or a galvanometer) included in this circuit measured the total current emitted by the filament. In one case the remaining electrodes H and A were maintained at the same potential as G, so as to cause electronic-molecular encounters to occur in a region where the bombarding electrons suffer no change of velocity except that due to their collisions with the gas. In the other case a difference of potential was applied between G and H in such a direction as to oppose the progress of electrons from the filament to the gauze H. By making this difference of potential larger than that applied between F and G, and including a sensitive galvanometer in the circuit between G and H, a measure of the ionization current corresponding to any value of the electron energy could be obtained. The former arrangement is preferable when it is desired to determine what are the minimum electron energies required for the production of particular spectrum lines, but the latter arrangement is a ready means of determining, in a qualitative manner, whether different parts of a spectrum require different amounts of energy for their excitation: for where such differences occur, the column of glow extending for part of the distance between G and H can be made to show different colours at different distances below G.

The value of the electron energy for any given value of the applied potential difference accelerating the electrons from the filament was obtained by adding to the applied potential difference a correction which was determined in each case by the methods which we have indicated in the former papers already referred to.

The two forms of apparatus used in the spectroscopic investigation were connected together and were supplied with hydrogen from the same storage bulb. The arrangements for circulating the pure gas through the apparatus were the same as those employed in our earlier investigations. The hydrogen entered the discharge tubes through a U-tube containing coconut charcoal and immersed in liquid air.

Fig. 2 is a diagrammatic representation of the apparatus used for the investigation of the origin of the radiations produced at the various critical voltages. It consists of two vertical discharge-tubes connected by a short horizontal tube. The two tungsten filaments, which are the sources of the bombarding electrons, are at F and H, the former, F, being situated at the bottom of the main tube (on the right-hand side of the figure), and the latter, H, at the top of the side tube. All the other electrodes are of platinum and are arranged as shown in the diagram. For convenience of reference, the electric fields between adjacent electrodes will



be referred to as V_1 , V_2 , etc., as indicated in the figure. The design of the apparatus makes it impossible for any radiation produced in the space between the gauzes K and L to illuminate the collecting electrode A or the electrode B directly, and it reduces to a minimum the possibility of radiation which originates between K and L being reflected by the glass walls and metal parts of the apparatus so as to illuminate A or B. The extent to which such radiation was reflected round so as to illuminate A or B was investigated by special experiments. These were carried out by using the general X-radiation produced by electronic bombardment of the gauze K in the highest obtainable vacuum, and by investigating the effect produced by this radiation

on the electrodes A and B when the electric fields were so arranged that no electrons or positive ions, which might possibly be knocked out of the various gauzes by bombardment, could reach the collecting electrode A. It was found that, even when the filament H was heated to the limit of safety and a very considerable amount of radiation was being produced in the side tube, no photo-electric effect of this radiation on either A or B could ever be detected. On the assumption that a given electron emission from the side filament H, with a given energy of bombardment, produces the same amount of radiation as an equal emission from the lower filament F does under the same applied potential difference, it was possible to estimate what fraction of the amount of radiation produced would have to be reflected round in order to give a detectable effect. By using an electron current from the lower filament equal to the maximum electron current ever used from the side filament, it was found in this way that if any radiation were reflected round so as to illuminate A, such reflected radiation was less than 1 part in 100,000 of that produced.

The hydrogen used in the experiments was prepared by the electrolysis of a solution of barium hydrate in water, and was dried before it entered the storage bulbs by passing it through a little coconut charcoal in a U-tube immersed in liquid air. The gas was admitted to the apparatus of fig. 2 through a coconut charcoal tube, cooled in liquid air, attached to the discharge tube shown on the left-hand side of the figure, and it could be pumped out through a similar U-tube connected to the main tube of the apparatus. In some of the experiments the gas was slowly streaming through the apparatus during the observations.

Before admitting hydrogen to any of the discharge tubes the residual gas was removed as completely as possible from the electrodes and glass walls by prolonged heating and pumping with a mercury vapour pump, the filaments being maintained glowing during the process.

Location of Critical Electron Energy Values.

The values of the critical electron energies for the production of radiation and of ionization in hydrogen were first carefully investigated by means of the apparatus indicated in fig. 2, using electrons from the lower filament F, and varying the energy of these by gradually increasing the field V_1 . Series of observations of the currents to various electrodes were taken for different values of V_1 with three

different arrangements of electric fields, which may be designated as arrangements for obtaining (a) Radiation, or R, curves, (b) Curves distinguishing between ionization and radiation, or (I—R) curves, (c) Inelastic collision curves. In taking observations of the type (a) or (b), the potential difference V_2 was arranged so as to oppose electrons from the filament, its value remaining constant during any one set of observations, but varying in different experiments from zero to 20 volts. The electrons from the filament encountered a larger constant retarding difference of potential in the space between the gauzes C and B, and were prevented from reaching the level of B. This difference of potential, V_3 , tends, of course, to drive any positive ions produced between B and C, or any which diffuse into this space from below, towards the gauze B. In arrangements for obtaining R curves, the field V_4 was made larger than $(V_2 + V_3)$ and was in the reverse direction to these fields, so as to prevent any positive ions from reaching the collecting electrode A. Any photo-electrically active radiation produced by the collisions of electrons with gas molecules would cause electrons to leave the upper surface of the gauze B and the attached cylinder, which are negatively charged with respect to A. Hence the only current reaching the collecting electrode in such circumstances is that carried by these photo-electrons from B. Discontinuities in the current-potential difference curves obtained with this arrangement of fields therefore indicate the critical values of the electron energy at which different types of collision resulting in the emission of radiation occur.

For obtaining (I—R) curves the only respect in which the arrangement of fields differed from that already described was that the difference of potential V_4 was very much smaller (about 2 volts or less). Such a small difference of potential would not prevent the positive ions which passed through the gauze B from reaching A and charging the electrometer positively, but it would still cause the photo-electric effect of the radiation to result in a charging of the electrometer negatively. Curves taken with such an arrangement of fields therefore indicate critical electron energies at which radiation is produced, by discontinuities at which inflexions towards the negative direction occur, while critical electron energies at which ionization is produced disclose themselves by discontinuities at which inflexions towards the positive direction occur.

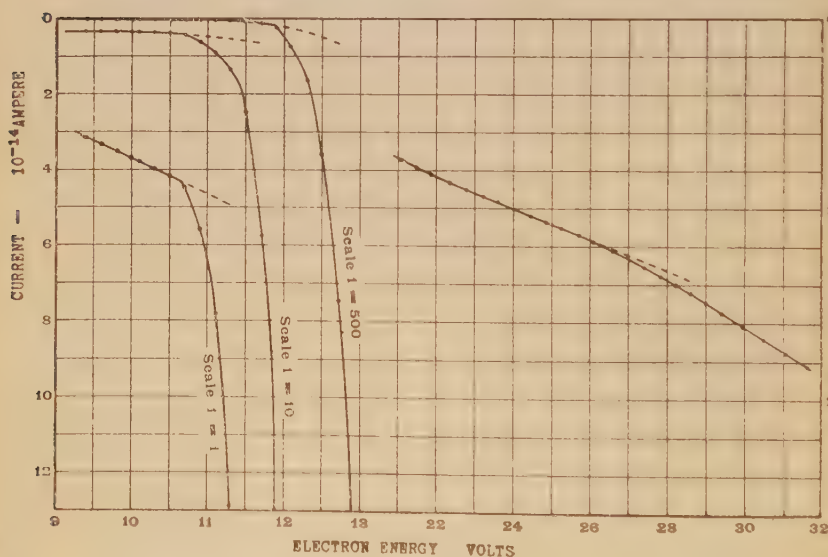
In the arrangement of electric fields for obtaining inelastic collision curves the gauzes D and C were maintained at the

same potential and a small difference of potential (1 volt or less) tending to prevent electrons from reaching the level of B was applied between C and B. Any electrons which reached this level in spite of the opposing potential difference, and which passed through the spaces of the gauze, were driven back on to the upper surface of this gauze by a difference of potential applied between A and B. A sensitive galvanometer included in the circuit between C and B therefore gave a measure of the electron current which reached the gauze B, and another galvanometer included in the circuit between F and D measured the thermionic emission from the filament.

Fig. 3.—R curves.

Pressure 0.047 mm.

Pressure 0.148 mm.



The curves given in figs. 3, 4, and 5 illustrate the indications of critical electron energies which were obtained by these methods. The curves shown in fig. 3 were obtained with the R arrangement of electric fields. They indicate three critical electron energies at which different types of collision occur between electrons and hydrogen atoms or molecules, which result in the production of radiation. The mean values of these critical points, taken from a large number of observations at pressures ranging from 0.002 mm. to 1 mm., are 10.2 volts, 11.9 volts, and 26.1 volts. Some

of the radiation curves suggested the existence of another critical electron energy for the production of radiation at about 12.5 volts, but the most conclusive evidence on this point was obtained from the $(I-R)$ curves. The first radiation bend in fig. 3 is at 10.7 volts. This is because the corrections for the critical points which are indicated in this figure were found not to be the same, the lower critical point requiring a correction 0.4 volt smaller than the second critical point. Hence the voltage interval between these two corrected radiation values is not accurately represented by the interval between the two bends in the observed current-voltage curves. The electron energies marked as abscissæ in fig. 3 are those obtained by the application of the correction which was found for the second critical point to all the potential differences applied between F and D (fig. 2), so that the lower critical voltage appears too high in the curve.

The appropriate corrections to add to the measured voltages for investigations when the R and $(I-R)$ arrangements of fields were employed was found by the "effect correction method" which the authors used in the case of neon*. It was determined by controlling, by means of a retarding potential difference V_1 , the number of electrons which were allowed to pass into the space between D and C (fig. 2), where the potential difference V_2 which was applied was sufficient to allow them to acquire the necessary energy for making collisions of the type under investigation, and by finding the maximum value of V_1 which would allow of the passage of a sufficient number of electrons to give a detectable indication of the effects of the collisions in as nearly as possible the arrangement of fields employed in obtaining the curve for which the correction was required. This maximum value of V_1 is the amount which has to be added to the measured differences of potential in the actual series of observations. The fact that the maximum value of V_1 (opposing electrons) at which a measurable photo-electric effect could be obtained, when the potential difference V_2 enabled the electrons to acquire energy in excess of about 11.9 volts, was larger than when the electrons were only able to acquire energy between 10.2 volts and 11.9 volts, indicates that a smaller number of electrons is necessary to produce a measurable photo-electric current if their energy exceeds 11.9 volts than if their energy is smaller than this amount. This, in itself, is evidence in support of the

* Proc. Roy. Soc. A, xcvi. p. 124 (1920).

genuineness of 11.9 volts as a critical energy stage, but in order to be quite sure that the bend in the radiation curve at 11.9 volts is not to be attributed to some peculiarity of the velocity distribution curve, the following procedure was adopted:—A series of observations was taken with the fields arranged for an R curve, and the “effect correction” was determined. A series of readings was then taken of the total thermionic current between F and D (fig. 2) for a series of values of V_1 arranged so as to oppose electrons from the filament. From these two sets of observations the values of the ratio of the photo-electric current to the corresponding effective thermionic current were calculated, using the results of the effect correction determination as the criterion for deciding which values of the thermionic current and of the photo-electric current are corresponding. The values of this ratio were plotted against the values of the electron energy deduced from the R series of observations, and it was found that this ratio increased steadily up to between 11.5 volts and 12 volts, after which it increased much more rapidly, thus showing that there is really a critical energy value in this region. The ratio curve had the same form whether the effect correction used was the one corresponding to the lowest, or the one corresponding to the second, of the critical points in the R curve, although, as might be expected, the position of the bend in the curve varied slightly according to which correction was used.

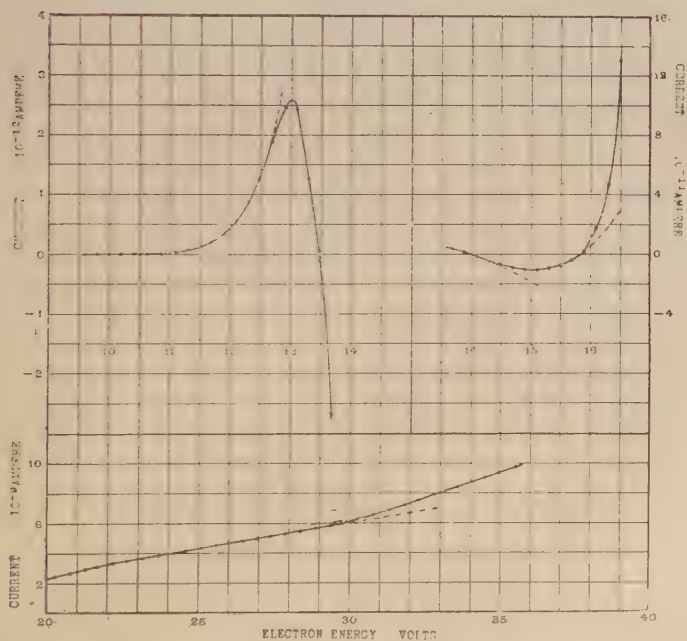
The determination by the effect correction method of the appropriate correction to apply in the case of the higher critical points, *e.g.*, that occurring at 26.1 volts in the radiation curve in fig. 3, and the ionization point shown at 29.4 volts in fig. 4 (see below), is complicated by the presence of the effects which occur at the lower energy stages. In these cases, therefore, the values have been corrected by the application of the same correction as was found necessary at the 11.9 volts and the 15.9 volts stages, for, as will be seen later, it seems probable that the higher critical values are connected with the same system as the 11.9 volts and the 15.9 volts values.

Fig. 4, which shows curves taken with the (I – R) arrangement of electric fields, confirms the suggestion of the existence of a critical energy value for the production of radiation at about 12.6 volts, and shows in addition four ionization points. The mean values of these ionization points, deduced from many series of observations, are:—10.5 volts, 13.6 volts, 15.9 volts, and 29.4 volts. As in the case of the 10.2 volts radiation point, the correction for the

10.5 volts and the 13.6 volts ionization stages was found to be 0.4 volt lower than the correction for the 15.9 volts stage, so that the interval between the ionization points in fig. 4 is not accurately represented in the curves, the two lower ones appearing to be too high. In many of the (I—R) curves no indication of the existence of an ionization energy at 13.6 volts was obtained, presumably because the amount of

Fig. 4.—(I—R) curves.

Two upper curves at 0.048 mm. pressure; lower curve at 0.180 mm. pressure.



ionization which is produced at this stage is very small, and, in the presence of the photo-electric current produced by the radiation, is only detectable for certain arrangements of the electric fields (*e. g.*, with a large value of V_2 tending to drive positive ions towards the collecting electrode).

In view of the fact that the curves in fig. 3 indicate the existence of two critical radiation stages below 12.6 volts, it is interesting to note that in the (I—R) curves 12.6 volts is the first critical radiation stage indicated, and that positive ions are detected between 10.5 volts and 12.6 volts. At

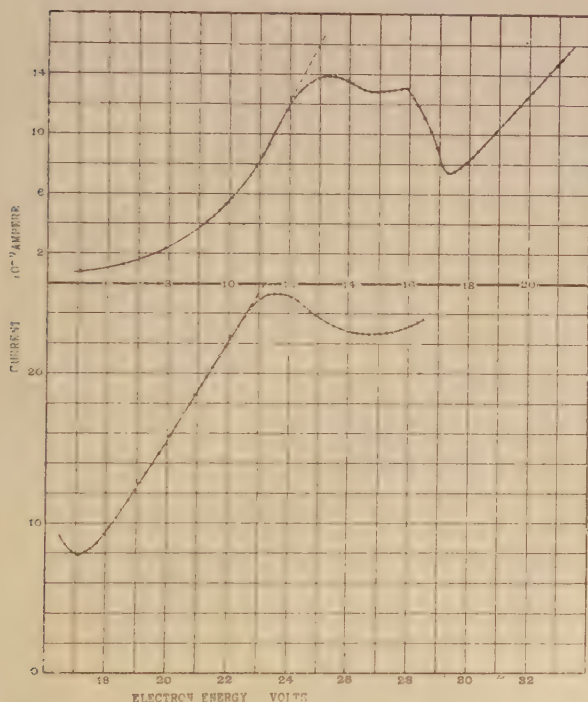
higher pressures (0.3 mm. or more) the positive current measured at this stage was very much smaller, and in some cases a small negative current was detected between 10.5 volts and 12.6 volts, in circumstances when the sharpness of the inflexion at 15.9 volts made it clear that the non-detection of positive ions could not be attributed to their failure to reach the collecting electrode. This suggests that the positive ions whose presence has been detected between 10.5 volts and 12.6 volts are not to be attributed to ionization of the hydrogen itself, but to some spurious effect, such as the production of positive ions by the electronic bombardment of the gauzes, or the ionization of a small trace of gaseous impurity. In this connexion it must be mentioned that at this stage of the research in (I—R) curves, taken in the best vacuum which we could maintain, with liquid air on and the diffusion pump working, a positive current of the same order of magnitude as that obtained with hydrogen in the apparatus began to be detected at 10.5 volts, and increased with increasing energy of the bombarding electrons. On first consideration it perhaps appears that this detection of a similar current in a "high vacuum" curve shows it to be due to electronic bombardment of the platinum gauze, but against such a conclusion must be set the fact that, in the earlier stages of the use of this apparatus, high vacuum observations of the same type showed that a very much smaller positive current was obtained for about the same electron emission, and that this effect of the bombardment of the platinum gauze did not commence before about 13 volts. As regards the second alternative, viz., ionization of a trace of impurity, the fact that the positive current was first detected at about 10.5 volts seems to point to the conclusion that, if such impurity is present, it is mercury vapour, for 10.4 volts is the value of the ionization potential for mercury. As, however, the carbon purifying tube was immersed in liquid air throughout the observations, the amount of mercury vapour present in the apparatus must have been very small. In a spectroscopic investigation of helium by one of us, the presence of the mercury line $\lambda 5461$ was, however, detected when similar precautions had been taken to exclude mercury*, so that the possible presence of a trace of the vapour in the present experiments cannot be ruled out on the grounds of the precautions taken to prevent its entry. Some of the (I—R) curves showed a bend in the curve at 11.9 volts, indicating that ionization increases more rapidly after this voltage is passed. This can be accounted for, if there is any system

* A. C. Davies, Proc. Roy. Soc. A, c. p. 599 (1922).

present whose ionizing potential is less than the voltage corresponding to the radiation which is emitted at 11.9 volts, as being due to the ionization of that system by the radiation instead of simply by direct electronic collision. Olmstead † came to the conclusion that the hydrogen molecule was itself ionized without dissociation at 11.4 volts, but, as will be seen

Fig. 5.—Inelastic collision curves.

Pressure 0.179 mm.



later, the results of the spectroscopic investigation do not support such a view. The form of the (I - R) curves between 10 volts and 13 volts will be referred to again when the origin of the various radiations is considered.

Fig. 5 shows the results obtained by the inelastic collision method. Three clear indications of inelastic collisions were found, the first at 11.9 volts, the second at 15.9 volts, and the third at 22.8 volts, and the definiteness of the bends in the curves at these stages must indicate that these three critical

† *Loc. cit.*

values are connected with encounters between electrons and hydrogen molecules. If dissociation of the hydrogen molecules could be produced by their encounters with electrons having 3.5 volts energy (Langmuir's value for the work of dissociation of the hydrogen molecule), the inelastic collision curves would be expected to show a decrease in the number of electrons reaching the gauze B at this value of the electron energy. Curves of the results obtained with small electron energies indicate, however, that dissociation by such low voltage electrons does not take place. By plotting the graph of the ratio of the current reaching the gauze B to the total thermionic emission, against the values of the electron energy, it was found that this ratio increased very considerably as the energy of the electrons was increased from about 8 volts to 10 volts. A possible explanation of this is that the hydrogen molecules have an affinity for electrons, and that those electrons which have less energy than that corresponding to a fall through about 8 volts tend to be captured by molecules, the resulting ions being more readily stopped by a small retarding difference of potential than are the free electrons.

By varying the magnitude of the potential difference V_3 opposing the electrons, and by various modifications of the method, attempts were made to obtain, in curves of this type, an indication of the existence of two critical energy values as close as 11.9 volts and 12.6 volts, but none of these attempts were completely successful. This was probably due to the fact that the range of energies among the bombarding electrons was greater than the difference between 12.6 volts and 11.9 volts. It seems possible, however, that the fact that the flattening of the curve, which commenced at 11.9 volts, generally extended over a longer voltage region than the steep drop in the curve, which commenced at 15.9 volts, is to be attributed to there being two inelastic collision points fairly close together near 11.9 volts and only one at 15.9 volts. The flattening of the curve which commenced at 22.8 volts generally extended to about 27 volts, however small V_3 was made, and no indication of another fall in the current at 26.1 volts, or at 29.4 volts, was obtained. In fact at 29.4 volts the current generally began to increase more rapidly than before with increasing voltage. The curves which the authors obtained in hydrogen by the inelastic collision method are very similar to those obtained by Mohler and Foote in the same gas*. These investigators

* F. L. Mohler and P. D. Foote, *Sci. Papers, Bur. of Stan.* 400, p. 669 (1920).

obtained a very definite bend in their curves in the neighbourhood of 21–22 volts*, and they interpreted this bend as being a multiple effect due to the occurrence of two inelastic collisions of a lower energy value, though they state that the possibility of the bend being due to a new type of inelastic collision is not excluded by their work. The authors think that the results which they themselves obtained cannot be accounted for by multiple collisions, for the steepness of the drop in the current at 15.9 volts shows that a very considerable proportion of the bombarding electrons make collisions of the 15.9 volts type, and this being the case it seems improbable that when the electron energy is increased the electrons cease to make collisions of the 15.9 volts type and make instead two successive collisions of lower energy value. The authors therefore take the view that the bend in the curve at 22.8 volts indicates the occurrence of a new type of inelastic collision, though it is possible that the extent of the fall in the current over such a considerable voltage region may be accounted for by some of the electrons making two collisions of the 11.9 volts type or of the 12.6 volts type, or one of each of these types. That this possible multiple collision effect is not the main factor is evidenced by the fact that the R and $(I - R)$ curves do not show an increased rate of production of radiation or of ionization at 22.8 volts. The absence of such an increased production of radiation or of ionization at a stage where undoubtedly an inelastic collision is occurring can only be accounted for on the supposition that the results of the new type of collision are of the same kind as the results of the last preceding type of inelastic collision, *i. e.*, in this case, that they are the same as those occurring at the 15.9 volts collision at which ionization is known to take place. Moreover, it must be the same system which is being ionized at the two critical points, but being ionized in a different way in the two cases. It is clear that the two values are to be attributed to electronic-molecular encounters because of their prominence in the inelastic collision curves, and it is possible that at one stage the process $H_2 \rightarrow H_2^+ + \text{electron}$ takes place, while at the other the process $H_2 \rightarrow H + H^+ + \text{electron}$ occurs, for then no increase in the number of positive charges per collision would result from the change. The value 22.8 volts is in fair agreement with that which Pauli has recently deduced, on theoretical grounds, as the voltage at which the process $H_2 \rightarrow H_2^+ + \text{electron}$ might be expected to occur. The value which he actually gave was 23.7 volts, but this

* Mohler, Foote, and Kurth, in the *Phys. Rev.* xix. p. 414 (1922), give this point as 22.3 volts.

involved the use of an experimental value of Franck's which the latter has since found should be reduced by 0.8 volt, so that Pauli's value becomes 22.9 volts. As will be seen later, the spectroscopic evidence indicates that the process of ionization of the molecule which occurs at 15.9 volts must be of the type $\text{H}_2 \rightarrow \text{H} + \text{H}^+ + \text{electron}$, because of the appearance of Balmer series lines in the spectrum at this voltage, so that the results of this investigation may be said to provide some experimental confirmation of Pauli's views.

The smallness of the effects occurring at 10.2 volts and at 13.6 volts in the R and (I-R) curves, combined with the absence of bends at these points in the inelastic collision curve, suggests that these critical values are to be attributed to collisions between electrons and hydrogen atoms and not to electronic-molecular encounters. A small proportion of atomic hydrogen might be expected to be present in the near neighbourhood of the filament, caused by temperature dissociation, but it would not be expected that the collisions of the hydrogen atoms with electrons would be sufficiently numerous to cause an appreciable reduction in the number of electrons reaching B in an inelastic collision curve, although the effects of the collisions (radiation or ionization) might be detectable if no other radiation or ionization were present. These two critical energy values are therefore taken to be the radiation and ionization voltages respectively, of the hydrogen atom: the values are in good agreement with those deduced from Bohr's theory.

With regard to the critical values which have been found at 26.1 volts and at 29.4 volts, the magnitude of the effects occurring at these stages, compared with the magnitude of the previously existing effects, must be taken to indicate that these values are to be associated with electronic-molecular encounters, even though no indication of inelastic collisions is found at these voltages in inelastic collision curves. The absence of such indications is probably to be explained by the fact that, as these energy values are approached, the number of ways in which the bombarding electrons may lose energy is so considerable that many electrons are already being prevented from reaching B, so that a change in the type of collision occurring does not result in a definite bend in the curve.

The only way in which the increased production of ionization at 29.4 volts can be accounted for is by supposing that two electrons are removed from the molecule at each inelastic collision. As it is inconceivable that the system H_2^{++} can exist alone, we are forced to the conclusion that 29.4 volts

corresponds to the work of dissociation of the molecule into two atoms and the ionization of both atoms. This conclusion is supported by the fact that the difference between 29.4 volts and 15.9 volts ($=13.5$ volts) agrees with the directly determined value of the ionization potential of the hydrogen atom. The energy required to dissociate the molecule must thus correspond to 29.4 volts $- 2 \times 13.5$ volts $= 2.4$ volts. This value does not agree with the value determined by Langmuir, but is in fair agreement with the value recently obtained by Olmstead. It will be noticed that 2.4 volts is the difference between two of the observed radiation energies, namely, 10.2 volts and 12.6 volts, which suggests that 12.6 volts corresponds to the dissociation of a molecule into atoms and the excitation of one atom. Evidence on this point is given by the experiments to be described in the next section.

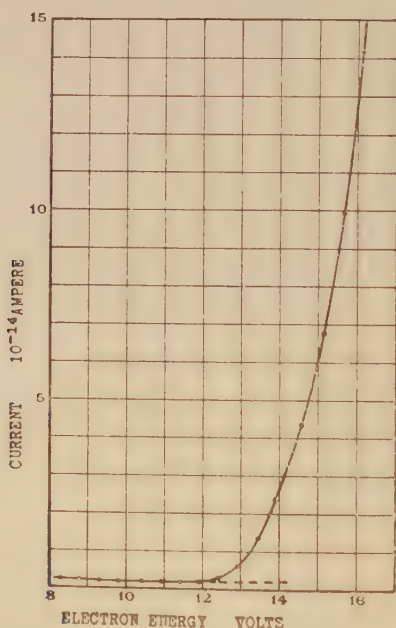
Investigation of the Origin of the Radiations.

The method by which this investigation was performed has already been briefly indicated. In order to insure that radiation was produced only in the space between K and L (fig. 2), the electrons from H were completely turned back in this space. The radiation produced in this space would, of course, act photo-electrically on all the negatively charged gauzes, and care had to be taken that photo-electrons so liberated were not able to acquire sufficient energy to enable them to give rise to radiation on collision with gas molecules in a region where such radiation could illuminate A or B directly. The fields V_7 , V_8 , and V_2 were therefore all small; V_7 was about 3 volts opposing positive ions, while V_8 was about 4 volts tending to prevent electrons from reaching D. V_2 was about 2 volts and was in a direction accelerating electrons from C to D. V_3 was larger than $(V_6 - V_7 + V_8 + V_2)$, the potential difference accelerating positive ions knocked out of the gauze K, and so prevented any positive ions from reaching the collecting electrode. V_1 was made smaller than V_3 , with the gauze B positive to the collecting electrode, *i. e.*, opposite in direction to V_3 . The photo-electric effect of radiation would therefore cause electrons to leave A and a positive current to be measured. If any electrons were knocked out of the gauze C by the positive ions turned back in the V_3 space, these electrons would be enabled, by means of the potential difference V_3 , to acquire sufficient energy to produce radiation. As, however, V_4 was only about 2 volts, these electrons would be able to reach A in spite of having

made collisions, and would give a negative current which would inevitably be larger than the positive current resulting from any radiation which they produced. The detection of a positive current with such an arrangement must therefore indicate that radiation produced in the space between the gauzes K and L has been passed on by the processes of absorption and re-emission by the gas. With hydrogen in the apparatus it was found that a positive current commenced when the electron energy was about 12 volts (see fig. 6), and

Fig. 6.—Radiation from side filament.

Pressure 0.094 mm.



that this positive current increased steadily with increase of the energy of the electrons. The magnitude of the photo-electric current measured at 13 volts indicated that the amount of radiation which passed round was about 1 part in 7000 of that produced in the side tube, an amount which is considerably more than could possibly be accounted for by reflexion.

Many series of observations of the current to the collecting electrode for gradually increasing electron energies were taken, and the resulting curves when plotted showed only the one bend at 12 volts, so that it seems probable that only one of the various types of radiation which are produced is capable of being handed on by the processes of absorption and re-emission. Even when the side filament was heated to the limit of safety no photo-electric effect was ever obtained in the main tube for values of the electron energy less than about 12 volts. Hence it must be the radiation which is produced at the 11.9 volts critical stage which can be passed on in this way. Radiation which comes round from the side tube must be produced by the excitation of a molecule without dissociation, so that the effect occurring at the 11.9 volts critical stage is evidently the genuine excitation of the molecule and the production of true molecular radiation. The radiation emitted at this stage is thus connected by the quantum relation with the critical voltage 11.9, and it would therefore be able to ionize mercury vapour (ionizing potential 10.4 volts) if this were present, as has been suggested. The sharp inflexion towards the negative direction at 12.6 volts in the ($I-R$) curves from the lower filament (see fig. 4) must indicate that the radiation produced at 12.6 volts, unlike that produced at 11.9 volts, is not able to ionize the gaseous impurity whose ionizing potential is about 10.5 volts. This supports the conclusion drawn from the radiation curves from the side filament, that the radiation produced at 12.6 volts does not correspond to the genuine excitation of the molecule, and, moreover, it affords strong confirmation of the suggestion that dissociation of the molecule into atoms, and atomic excitation of the 10.2 volts type, occurs at this stage, for radiation corresponding to only 10.2 volts would be unable to ionize a substance whose ionizing potential was 10.5 volts, and its effect would therefore appear in the curve as a radiation (or negative) current, and not as an ionization (or positive) current.

With regard to the critical electron energy for the production of radiation which was indicated in the R curves from the lower filament at 26.1 volts (fig. 3), no corresponding increased production of photo-electric current was found at the same stage in the radiation curve from the side filament, so that we are led to the conclusion that the process which occurs at this voltage results in an increase of atomic radiation and not in an increase of true molecular radiation. It seems probable that the process which occurs is the

following :— $\text{H}_2 \rightarrow \text{H}^+ + \text{electron} + \text{H}^{(\text{excited})}$, which would require $(2.4 + 13.5 + 10.2)$ volts = 26.1 volts.

Results of the Spectroscopic Investigation.

For the purposes of the present paper it is sufficient to consider the results of the spectroscopic investigation simply in so far as they throw light on the various ionization and excitation stages already referred to. The complete account of the spectroscopic investigation must be deferred to another paper. It may be stated at once that it was not found possible to excite the secondary spectrum lines at one voltage and the lines of the Balmer series at another voltage. Moreover, in no circumstances were any lines observed below the ionization potential 15.9 volts, either with or without the magnetic field to concentrate the luminosity, though the Balmer series lines and the brighter lines of the secondary spectrum were frequently observed within a few tenths of a volt of this value. If ionization of the hydrogen molecule occurred at 11.9 volts (or at 11.4 volts as Olmstead suggests) it would be expected that some, at any rate, of the secondary spectrum lines could be obtained at voltages slightly higher than this. Therefore the absence of lines may be taken as evidence that no such ionization does occur.

The spectrum of the luminosity obtained in the form of apparatus indicated in fig. 1 differed from the spectrum of that obtained in the tungsten filament apparatus with the movable anode, in that many more lines of the secondary spectrum were visible in the former than in the latter, and that altogether the secondary spectrum was very much brighter in relation to the Balmer lines in the former case than in the latter. This is doubtless to be attributed to the occurrence of a relatively greater amount of temperature dissociation of the hydrogen in the case of the tungsten filament apparatus than when the lower temperature coated platinum filament was employed. Using the apparatus indicated in fig. 1 it was found that on reducing the E.M.F. after having once obtained a bright glow, the brighter secondary spectrum lines could be seen after the Balmer series lines $\text{H}\alpha$ and $\text{H}\beta$ had faded out, though once these lines had ceased to be visible no further fall of potential difference between the electrodes accompanied the decrease of current until all the secondary spectrum lines had disappeared. It is therefore evident that increase of current density enhances

the Balmer series lines relatively to the secondary spectrum*, but that in normal molecular hydrogen the lines of the Balmer series and of the secondary spectrum are excited at the same electron energy, namely that equivalent to 15.9 volts. Thus the ionization process which occurs at this voltage must involve the dissociation of the molecule into atoms, and the ionization of one of these atoms. It seems probable that the enhancement of the Balmer series lines at the greater current densities is a consequence of the rise of temperature of the gas which results from the increased current through it.

A definite blue glow could be seen in the discharge tube even when no lines were visible. This blue glow could be produced at lower voltages than were required to obtain the Balmer lines or the secondary spectrum lines, and its spectrum was found to be a continuous one extending from the yellow right across to the violet limit of the visible region. The appearance of lines in the spectroscope as the voltage across the discharge tube was raised was accompanied by the presence of a distinct pinkness in the glow, and whenever the glow showed traces of this pinkness the brighter secondary spectrum lines could be distinguished through the spectroscope. By using a retarding difference of potential of a few volts between G and H (fig. 1) a bright column of blue glow could be obtained extending right across the space between these two gauzes with traces of pinkness just in the vicinity of the gauzes. The spectrum of the luminosity could then be seen to consist of the continuous spectrum from the yellow to the violet with faint traces of lines just at the top and bottom of the field of view. With the glow in this condition it required only a small increase in the applied potential difference between F and G to cause the luminosity to change suddenly to a bright pinkish column extending the whole way between G and H, whose spectrum showed most of the secondary lines together with $H\alpha$ and $H\beta$. By using a large retarding difference of potential between G and H, a stage could be obtained when, with the magnetic field on, the luminosity consisted of a short concentrated column just below G, with a distinctly blue tip at its lower end, and an outer sheath of pink glow around the part nearest G. Increasing the potential difference between F and G would then cause the pink sheath to extend downwards and shoot

* This effect has been observed by R. W. Wood (Phil. Mag. xlv. p. 538, 1922), in his investigations of the hydrogen spectrum in long vacuum tubes.

through the blue tip until it ultimately extended the whole way. As the voltage across the tube was reduced beyond the 15.9 volts stage, the blue glow remained plainly visible, though it gradually grew fainter until ultimately it could only be detected at the surface of the gauze. It could generally be seen at lower voltages in the absence of the magnetic field, and the lowest voltage at which it was definitely observed in the present investigation was 13.5 volts, though the gradual manner of its disappearance suggested that this was not necessarily a limiting value. Its agreement with the ionizing potential for the atom appears to be fortuitous, for no trace of the Balmer series lines could be seen in the blue glow even when it was at its brightest. Moreover, with this apparatus with its low temperature source of electrons, no ionization commencing at 13.5 volts was detected. The authors think it probable that the true limit for the production of the blue glow is at 12.6 volts, the stage at which they have concluded that dissociation of the hydrogen molecule into atoms and the simultaneous excitation of one of each pair of atoms occurs, for it seems not improbable that a continuous spectrum would arise from the formation of molecules by the combining together of neutral atoms, and these would be produced for the first time at 12.6 volts. If diatomic molecules alone were formed it might be expected that the long wave-length limit of the resulting continuous spectrum would correspond to the energy of dissociation of the normal molecule, which the present research has indicated as being 2.4 volts. Although the exact determination of the long wave-length limit of the continuous spectrum of the blue glow could not be performed with a high degree of accuracy, there can be no doubt that the spectrum extended on the red side well beyond the wave-length corresponding to 2.4 volts, so that it is possible that part, at any rate, of this continuous spectrum is to be attributed to combinations resulting in the formation of some other system whose dissociation energy is less than that of H_2 , possibly the system H_3 .

The spectrum of the luminosity produced in the discharge tube was examined visually up to exciting voltages of about 15, but no evidence was obtained that fresh lines made their appearance at higher voltages, or that any lines already present disappeared as the voltage was increased beyond the stage at which a bright pinkish glow was first obtained.

This part of the investigation may therefore be said to have shown that ionized atoms are produced at the ionization stage at 15.9 volts, so that the process of ionization then

occurring must be $\text{H}_2 \rightarrow \text{H} + \text{H}^+ + \text{electron}$. If at 22.8 volts ionization occurs by the process $\text{H}_2 \rightarrow \text{H}_2^+ + \text{electron}$, the question arises as to whether new lines should be expected to make their appearance. Pauli thinks that the system H_2^+ ultimately breaks up into $\text{H} + \text{H}^+$ with an emission of radiation corresponding to the difference in the energies of the two systems, which would lie outside the visible region of the spectrum. If such a breaking up of the system H_2^+ occurs, the final products of the ionization are the same as at 15.9 volts, so that recombination would not be expected to give rise to additional lines. Unless the system H_2^{++} can exist alone, which is very unlikely, no new lines are to be expected to make their appearance at 29.4 volts when the double ionization occurs.

It is perhaps worthy of mention that in photographs of the spectrum of the luminosity taken at 23 volts, the following lines of Group II. of Fulcher's classification were among those present : $\lambda\lambda$ 5916·8, 5931·6, 5938·9, and 6028·2. The lines $\lambda\lambda$ 5916·8 and 6028·2 were placed by Fulcher in both groups, and their classification is therefore doubtful, but the other two lines belong definitely to Group II. The present observations therefore differ in this respect from those of Duffendack, for the latter did not observe any of the Group II. lines except those of doubtful classification, even with voltages as great as 40. The Fulcher Group II. includes those lines at the red end of the spectrum which Dutour found showed a Zeeman effect. Of the other lines which show the Zeeman effect several in the region λ 4660- λ 4800 are present on our plates, namely, $\lambda\lambda$ 4723·0, 4719·0, 4709·5, 4692·0, and 4673·1.

Summary of Principal Results.

The various lines of investigation have indicated that the critical energy values given below correspond to the following processes:—

Volts.		
10.2...	Atomic excitation	$H \rightarrow H^{(excited)}.$
11.9...	Molecular excitation	$H_2 \rightarrow H_2^{(excited)}.$
12.6...	Dissociation + atomic excitation	$H_2 \rightarrow H + H^{(excited)}.$
13.5...	Atomic ionization	$H \rightarrow H^+ + electron.$
15.9...	Dissociation + atomic ionization of one atom	$H_2 \rightarrow H + H^+ + electron.$
22.8...	Molecular ionization.....	$H_2 \rightarrow H_2^+ + electron.$
26.1...	Dissociation + atomic ionization + atomic excitation	$H_2 \rightarrow H^+ + electron$ $+ H^{(excited)}.$
29.4...	Dissociation + ionization of both atoms ...	$H_2 \rightarrow 2H^+ + 2 electrons.$

The results of the present experiments, while agreeing with those of the recent experiments of Olmstead with regard to the interpretation of the effects found to occur at the following voltages: 10.2, 12.6, 13.5, and 15.9 (Olmstead's values, 10.1, 12.9, 13.6, 16.0), differ from his results in regard to the critical energy stages found between 10.2 volts and 12.6 volts. Olmstead concluded that ionization of the hydrogen molecule occurs at 11.5 volts, and that the excitation of the hydrogen atom to the emission of the second line of the Lyman series occurs at 12.2 volts, whereas the present investigation has indicated only one critical energy value in this region, namely, 11.9 volts, at which it was found that radiation was produced from the molecule. This value is in agreement with the recent work of Mohler, Foote, and Kurth, who have deduced from their inelastic collision curves that there is a resonance potential at 11.8 volts, which they attribute to normal hydrogen.

The present experiments have established the existence of a genuine molecular radiation as distinct from a radiation produced by electronic-molecular encounters at which dissociation and atomic excitation occur. They have also provided a certain amount of experimental evidence in support of Pauli's suggestion that the production of positively charged hydrogen molecules requires energy equivalent to about 23 volts.

On the spectroscopic side the results of the experiments are in general agreement with those of Duffendack, except for the observation of certain lines of Group II. of Fulcher's classification, which were not detected by Duffendack at similar voltages. In addition, the experiments have shown that a visible continuous spectrum of hydrogen can be produced in the absence of the Balmer series lines and the lines of the secondary spectrum, and it is concluded that this continuous spectrum arises from the formation of molecules (H_2 , or possibly H_3) by the combination of neutral atoms.

The authors are indebted to the Radio Research Board of the Department of Scientific and Industrial Research for the means of purchasing some of the apparatus used in this investigation.

XCV. *Absorption Measurements of the Change of Wave-Length accompanying the Scattering of X-Rays.* By ARTHUR H. COMPTON, *Wayman Crow Professor of Physics, Washington University, Saint Louis* *.

IN some recent papers † the writer has described spectroscopic experiments which have shown that when the characteristic X-rays from molybdenum are scattered by graphite, the wave-length of the X-rays is increased. While these spectroscopic investigations have been made for only two wave-lengths, 708 and 630 Å., a quantum theory of the phenomenon has been developed ‡ which predicts that a similar change in wave-length should occur whatever the wave-length of the primary beam. Absorption measurements on scattered γ -rays have indicated a change in wave-length of about the theoretical amount §, but interferometer measurements on light scattered by paraffin have failed to show any effect of this character ¶. Apparently, therefore, the change in wave-length due to scattering depends in some way upon the wave-length of the primary radiation used. The present experiments, in which the change in wave-length was measured by an absorption method, have as their primary object to test the theory over a wider range of wave-lengths, and for a greater variety of scattering materials than could be done conveniently by the spectroscopic method.

The quantum theory of this change in wave-length is based upon the hypothesis that each quantum of primary X-rays is scattered by an individual electron. If the frequency of the incident quantum is ν_0 , its energy is $h\nu_0$, and its momentum is $h\nu_0/c$, where c is the velocity of light. Due to the change in direction of the quantum on scattering, its momentum is altered, resulting in a recoil of the scattering electron. Equating the momentum of recoil of the electron to the change in momentum of the quantum, we have,

$$\left\{ \frac{m\beta c}{\sqrt{1-\beta^2}} \right\}^2 = \left(\frac{h\nu_0}{c} \right)^2 + \left(\frac{h\nu_\theta}{c} \right)^2 + 2 \frac{h\nu_0}{c} \frac{h\nu_\theta}{c} \cos \theta. \quad (1)$$

* Communicated by the Author.

† A. H. Compton, Bulletin National Research Council, xx. p. 16 (Oct. 1922); Paper before American Physical Society, April 28, 1923, Phys. Rev. June 1923; and Phys. Rev. xxii. (1923).

‡ A. H. Compton, Bull. N. R. C. xx. p. 18 (Oct. 1922); Paper before Am. Phys. Soc., Dec. 1, 1923; Phys. Rev. xxi. p. 207 (Dec. 1923) & xxi. p. 483 (May 1923). P. Debye, *Phys. Zeitschr.* xxviii. p. 161 (April 15, 1921).

§ A. H. Compton, *Phil. Mag.* (May 1921); Phys. Rev. xxii. (1923).

¶ P. A. Ross, *Science*, lvii. p. 614 (1923).

Here βc is the velocity with which the electron recoils, and ν_θ is the frequency of the rays scattered at the angle θ . But the energy of the scattered quantum is less than that of the incident quantum because of the energy spent in setting the scattering electron in motion. Thus,

$$h\nu_0 - h\nu_\theta = mc^2 \left\{ \frac{1}{\sqrt{1-\beta^2}} - 1 \right\} \quad . \quad . \quad . \quad (2)$$

Combining these two equations we find,

$$\nu_\theta = \nu_0 / 1 + \alpha(1 - \cos \theta), \quad . \quad . \quad . \quad (3)$$

where $\alpha = h\nu_0 / mc^2 = h / mc\lambda_0, \quad . \quad . \quad . \quad (4)$

or $\delta\lambda = \lambda_\theta - \lambda_0 = \gamma(1 - \cos \theta), \quad . \quad . \quad . \quad (5)$

where $\gamma = h / mc = 0.0242 \times 10^{-8} \text{ cm.}^* \quad . \quad . \quad . \quad (6)$

Typical results of the spectrum measurements of this change in wave-length are shown in fig. 1, which represents, for slits of two different widths, the spectra of the $K\alpha$ ray from molybdenum: (A) the primary ray, (B) as scattered by graphite at 45° , (C) as scattered at 90° , and (D) as scattered at 135° †. The line P is drawn in each case at the position of the primary line, and the line T at the theoretical position of the scattered line as given by equation (5). It will be noticed that, within a comparatively small probable error, the wave-length of one component of the scattered beam is exactly that predicted by this quantum theory. There remains, however, a part of the scattered beam which is unchanged in wave-length.

Experimental Method.

For the measurement of the difference in absorption coefficient between the primary and the scattered ray, a balance method was employed, as is shown diagrammatically in fig. 2. Two beams of X-rays from the target X of a Coolidge tube came through separate windows in the lead box. One of them was scattered by a radiator R into an ionization chamber I, and the other went directly through a slit of variable width S into a second ionization chamber I'.

* Since the mass of a quantum is $h\nu/c^2 = h/\lambda c$, the mass of a quantum of radiation of wave-length γ is $h/(h/mc)c = m$; i. e. a quantum of radiation of wave-length γ has a mass equal to that of the electron. This fact was pointed out to me by Dr. Eldridge through Prof. A. Sommerfeld.

† Cf. A. H. Compton, Phys. Rev. xxii. (1923).

One ionization chamber was kept at a positive and the other at a negative potential, so that with equal ionization currents

Fig. 1.

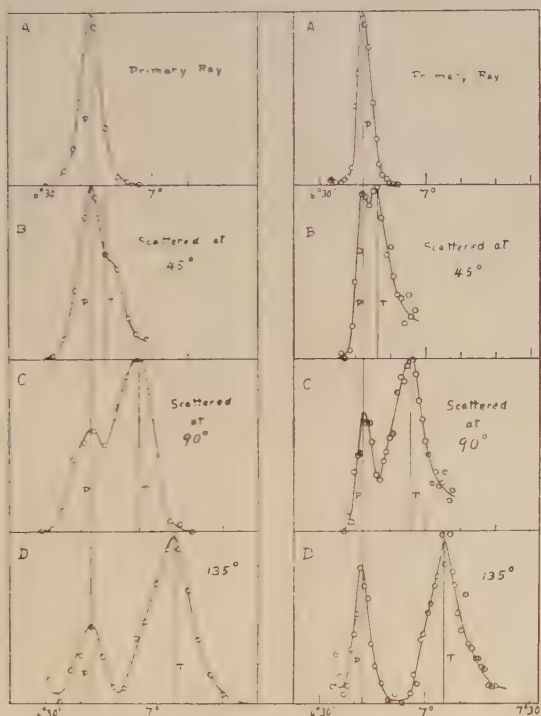
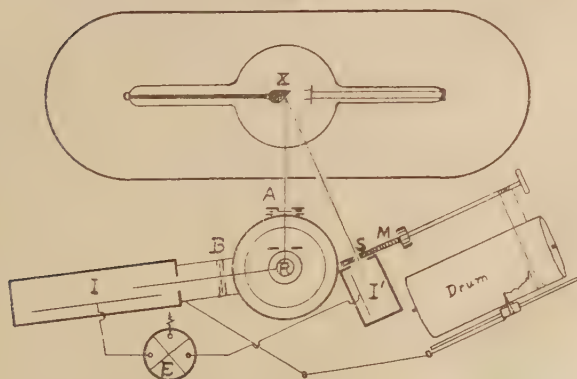


Fig. 2.



in each there was no deflexion on the electrometer E. The variable slit S was opened by a micrometer screw M.

The shaft driving this screw had wrapped about it a metal cord which was wrapped also about a drum in such a manner that the drum was rotated when the slit was opened by the micrometer screw. A recording pen moving along the drum was actuated by a metal cord fastened to the movable ionization chamber. Thus each position of the pen corresponded to a particular angle of the ionization chamber.

The chamber I was rotated through a range of angles of about 75° by a motor driving a worm gear. As the chamber was moving, the micrometer screw was turned so as to keep the electrometer at its zero position. In this manner a record was obtained on a sheet of paper placed around the drum showing the width of the slit for every angle of the

Fig. 3.

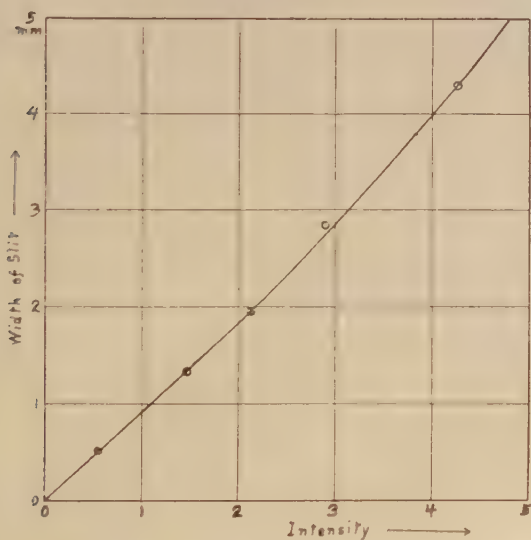


The scattering of hard X-rays by paraffin. In curve A_2B_1 , 2 mm. of copper are in the path of the primary beam and 1 mm. in the path of the scattered beam, and similarly for the other curves. The fact that the intensity is greatest with the absorbing screen in the path of the primary beam shows that the wave-length of the X-rays is increased by scattering. The curves were made in the order of their numbers.

chamber I. A record of this type, copied in indian ink for reproduction, is shown in fig. 3, which represents the scattering of hard X-rays by a block of paraffin. In this figure the ordinates represent the width of the slit-opening, and the abscissæ represent the angle of the ionization chamber.

To interpret the graphs thus obtained, it was necessary to determine how the ionization in the chamber I' varied with the width of the slit. This was done by means of a sector disk made of lead which cut off a known and adjustable fraction of the primary X-ray beam. A calibration curve taken in this manner is shown in fig. 4, where the intensity

Fig. 4.



of the ionization is plotted against the width of the slit in millimetres. It will be seen that for slit-widths less than 2 mm. the calibration curve is sensibly a straight line, and that the departure from such a line is not large even for the greater widths.

The X-rays scattered into the chamber I were filtered through an absorption screen placed at A or B. It was necessary to place a similar absorption screen in the path of the rays entering I' in order that slight variations in the voltage applied to the X-ray tube should not destroy the balance between the two ionization currents. Of course,

the beam entering the chamber I was much less intense than that entering the chamber I'. This difference in intensity was balanced by making the chamber I much larger and filling it with methyl-iodide vapour.

The change in absorption coefficient, corresponding to the change in wave-length of the scattered beam, was measured by observing the relative intensity of the scattered beam when an absorbing screen was transferred from position A to position B. If I_p is the intensity of the primary beam whose wave-length is λ and whose absorption coefficient in the absorbing screen is μ , and if S is the fraction of the energy of this beam which is scattered into the ionization chamber when no absorption screens are present, then the intensity of the scattered beam when a screen of thickness x is placed at A is $I_A = I_p S e^{-\mu x}$. If the absorption coefficient of the scattered ray is μ' , the intensity of the scattered ray when the screen is placed at B is $I_B = I_p S e^{-\mu' x}$. Thus

$$\frac{I_A}{I_B} = e^{(\mu' - \mu)x}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

whence

$$\delta\mu = \mu' - \mu = \frac{1}{x} \log (I_A/I_B). \quad . \quad . \quad (8)$$

It is clear from equation (7) that if μ' were equal to μ , I_A would be equal to I_B . If the absorption coefficient of each component of a complex beam of X-rays were unchanged by scattering, its intensity should therefore be unaltered by moving the absorbing screen from A to B. Hence the intensity of the whole beam should also remain unchanged. Thus any change observed in the intensity of the scattered ray when the absorption screen is shifted from position A to position B represents a change in the absorption coefficient of the component rays when the X-rays are scattered*. The fact, which is shown clearly by fig. 3, that the intensity of the rays is greater when the screen is at A therefore means that μ' is greater than μ †, that is, that each component of the X-ray beam is softened during the scattering process.

* This conclusion is strictly true only in case the fraction of the rays which is scattered from the absorber placed at A onto the radiator is the same as the fraction scattered from the absorber when placed at B into the ionization chamber. The apparatus was so designed that this condition was at least very nearly fulfilled. However, even if uncorrected, the error from this source would have been very small.

† It is by no means always true, when heterogeneous X-rays are used, that the scattered ray is softer than the primary ray. For if the radiator is of considerable thickness, the more penetrating parts of the primary beam are scattered by the whole radiator while the softer components

Knowing the absorption coefficient of the primary beam, and the change in absorption coefficient due to scattering, one can determine the wave-length of both the primary and the scattered beam. For this purpose I have employed the absorption data for different wave-lengths given by Hewlett, Richtmyer, and Duane*.

Experimental Results.

The results of these absorption measurements are collected in Table I., under the head of observer 2, and the corresponding wave-lengths are exhibited in Table II. In each case the scattering material was in the form of a cylinder, 2 cm. in diameter, with walls of such thickness that more than half of the X-rays were transmitted. The wave-length changes are very consistent with each other in every case except that of the secondary radiation from lead for the effective primary wave-length 0.14 Å. In this case the change in wave-length, especially at the small angles, is considerably greater than the theory predicts. The difficulty obviously lies in the fact that the fluorescent K radiation from lead is being excited in large amounts, and that this secondary radiation is always softer than the ray which excites it. The measurements of the scattering by the other elements for wave-lengths 0.12 and 0.13 Å. are also slightly affected by the fluorescent K radiation from the lead slits, the tendency being to make the observed change in wave-length greater at small angles and less at large angles with the primary beam, just as in the case of the scattering by lead. These fluorescent rays are not excited appreciably when the effective wave-length of the primary beam is

are absorbed before they have penetrated very deeply. Because of this filtering process, it usually happens that the scattered ray is more penetrating than the primary. One cannot help but feel that this process may account in part for the small magnitude of the change in absorption observed by Barkla and Miss Sale (Phil. Mag. xlv. p. 758, 1923), even though they took the precaution of using thin sheets of paper as radiators. Changes in absorption due to scattering similar to those described here have been observed for γ -rays by Eve, Phil. Mag. viii. p. 669 (1904); R. D. Kleeman, Phil. Mag. xv. p. 638 (1908); Madsen, Phil. Mag. xvii. p. 423 (1909); D. C. H. Florence, Phil. Mag. xx. p. 921 (1910), xxvii. p. 225 (1914); J. A. Gray, Phil. Mag. xxvi. p. 611 (1913); A. H. Compton, Phil. Mag. xli. p. 749 (1921); *et al.* For X-rays the change has been observed by Sadler and Mesham, Phil. Mag. xxiv. p. 138 (1912); J. Laub, *Ann. de Phys.* xvi. p. 785 (1915); J. A. Gray, Frank. Inst. Jour. p. 643, Nov. (1920); A. H. Compton, Phys. Rev. xviii. p. 96 (1921); Nature, cviii. p. 366 (1921); and J. A. Crowther, Phil. Mag. xlii. p. 719 (1921).

* These data are collected in Bulletin N. R. C. no. xx. p. 32 (1922).

TABLE I.
Mass Absorption Coefficients of Primary and Scattered X-Rays.

Radiator.	Absorber.	μ/p Primary.	$\delta(\mu/p)$, Scattered Ray.								Observer.
			30°.	45°.	60°.	75°.	90°.	105°.	120°.	135°.	
Paraffin	Pb	.07302771	1
Aluminum	Pb	.07302743	1
Iron	Pb	.0730371443	1
Tin	Pb	.07301725	1
Lead	Pb	.073	...	(?)08	1
Paraffin	Cu	.45	.043	.08	.12	.20	.245	.32	2
Graphite	Cu	.46	.08	.10	.12	.19	.15	.33	2
Aluminum	Cu	.45	.05	.08	.13	.19	.24	.30	2
Copper	Cu	.59	.04	.07	.10	.15	.19	.26	2
Lead	Cu	.64	.21	.27	.31	.32	.33	.34	2
Paraffin	Cu	.76	.065	.11	.17	.26	.34	.42	.50	.59	2
Graphite	Cu	.76105	.16	.23	.36	.46	.52	.59	2
Aluminum	Cu	.7610	.14	.21	.295	.35	.42	.53	2
Copper	Cu	.7606	.15	.20	.23	.32	.39	...	2
Tin	Cu	1.0307	.12	.17	.23	.36	2
Lead	Cu	1.0510	.14	.14	.19	.20	2
Paraffin	Cu	1.74	.09	.16	.29	.405	.52	.63	2
Paraffin	Cu	2.84	.15	.25	.33	.51	.60	.73	2
Paraffin	Cu	5.25	.17	.29	.50	.77	1.00	1.16	2
Paper	Al	.70-.9022	3
Paper	Al	1.15-1.8322	3
Paper	Al	1.90-4.4218	3
Paper	Al	4.8-10.307	3

greater than 0.15 \AA . The fluorescent K-rays from the copper absorbing screen would also have been a source of difficulty had not the differential absorption coefficients $\delta(\mu/p)$ been measured after the scattered rays had been

TABLE II.
(Change in Wave-Length Accompanying the Scattering of X-rays.)

Radiator.	λ , A.U., Primary.	$\Delta\lambda$ for Scattered Ray, A.U.								Observer.
		30°.	45°.	60°.	75°.	90°.	105°.	120°.	135°.	
Free electron	All.	.003	.007	.012	.018	.024	.030	.036	.041 Theory.	
Paraffin024006051	1
Aluminium024006039	1
Iron024007021029	1
Tin024004029	1
Lead024013	1
Paraffin12	.005	.010	.013	.020	.024	.031	2
Graphite12	.010	.013	.015	.021	.027	.033	2
Aluminium12	.006	.010	.015	.020	.025	.030	2
Copper13	.004	.007	.010	.014	.017	.022	2
Lead14	.016	.021	.024	.025	.025	.026	2
Paraffin15	.004	.008	.012	.018	.023	.027	.033	.039	2
Graphite15007	.012	.017	.025	.031	.034	.038	2
Aluminium15007	.010	.016	.021	.025	.028	.035	2
Copper15005	.011	.015	.017	.023	.027	...	2
Tin17004	.007	.010	.013	.020	2
Lead17005	.008	.008	.011	.012	2
Paraffin21	.004	.008	.014	.018	.023	.027	2
Paraffin25	.005	.008	.012	.017	.020	.024	2
Paraffin32	.003	.006	.010	.015	.020	.023	2
Paper30-33047	3
Paper41-50023	3
Paper50-69015	3
Graphite63020	4
Graphite71003018031	4
Paper70-90003	3

filtered through at least .5 mm. of copper. This precaution was sufficient also to eliminate the effect of the K-rays from tin when it was used as radiator.

For sake of completeness, I have included in Tables I.

and II. the results of some earlier experiments on γ -rays* (Observer 1), Barkla and Sale's recent experiments on the change in absorption coefficient of soft X-rays scattered by paper† (Observer 3), and my spectrum measurements on the change of wave-length of molybdenum K-rays‡ (Observer 4). In the case of the γ -rays, the wave-lengths are calculated from the absorption coefficients according to the equation $\mu/\rho = \tau/\rho + \sigma/\rho$, where § $\tau/\rho = 1.64 \times 10^3 \lambda^3$ and || $\sigma/\rho = .151(1 + .0485/\lambda)$. In Barkla and Sale's work, it did not seem possible to reproduce the results in successive series of experiments. I have accordingly averaged their results obtained for certain arbitrarily chosen ranges of wave-lengths, and have estimated the wave-lengths from Hewlett's data for the absorption of different wave-lengths in aluminium. The wave-length changes estimated from the spectrum measurements are the weighted mean values of the modified and the unmodified rays.

From Table II. it is apparent that in order that the scattered ray shall be changed in wave-length by the amount predicted by equation (5), X-rays of very short wave-length and radiators of low atomic number must be employed. These facts are exhibited in figs. 5 and 6. In fig. 5 is plotted the change in wave-length observed when X-rays of widely differing wave-lengths are scattered by paraffin¶. For both wave-lengths 0.024 and 0.15 Å., the observed change is very nearly that predicted by the theory (as represented by the solid curve); but the change for $\lambda=0.32$ Å. is slightly less, and that for $\lambda=0.71$ is still less than the theoretical value. Similarly in fig. 6, whereas the change in wave-length of the rays scattered by carbon is within experimental error that demanded by theory, the wave-length change for the heavier elements becomes less and less as the atomic number becomes greater. The difference here shown between the rays

* The value of μ/ρ for the primary γ -rays in lead is that of M. Ishino, Phil. Mag. xxxiii. p. 140 (1917), and for the scattered rays is from A. H. Compton, Phil. Mag. xli. p. 760 (1921).

† C. G. Barkla & Rhoda Sale, Phil. Mag. xlv. p. 748 (1923).

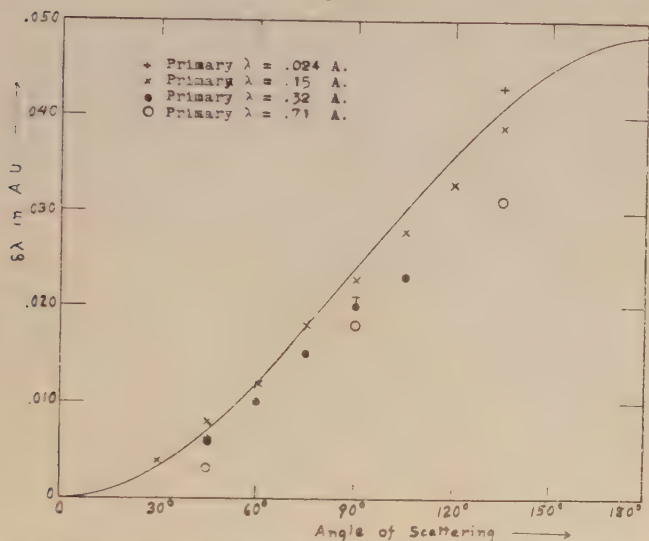
‡ For $\lambda=0.63$ (MoK β -line, cf. A. H. Compton, Phys. Rev. xxi. p. 495 (1923). For $\lambda=0.71$ (MoK α -line), cf. fig. 1 of this paper.

§ A. W. Hull & Marion Rice, Phys. Rev. viii. p. 836 (1916).

|| The mass absorption due to scattering, according to the writer's quantum theory (Phys. Rev. xxi. p. 493, 1923), is $\sigma/\rho = \sigma_0/\rho(1+2\alpha)$, where σ_0/ρ is the mass scattering calculated on the classical theory, and has the value 0.151.

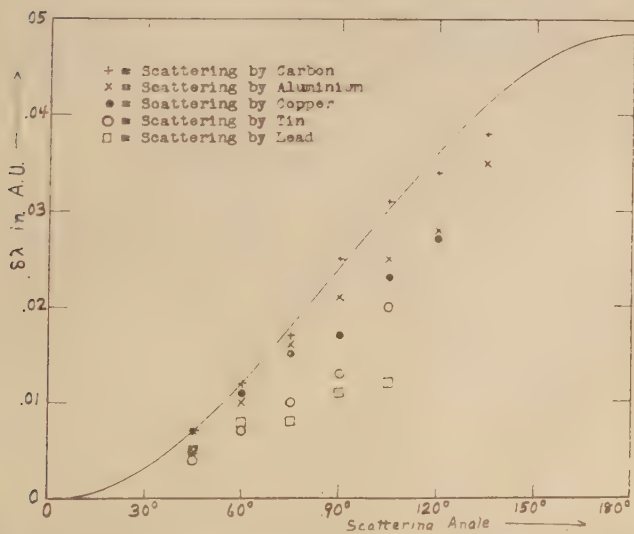
¶ In the measurements on γ -rays ($\lambda=0.024$ Å.), as plotted in fig. 5, the mean wave-length change for paraffin, aluminium, and iron is used, in order to reduce the probable experimental error. All of these elements may be considered as of low atomic number when γ -rays are employed.

Fig. 5.



The change in wave-length accompanying the scattering of X-rays by paraffin, when different primary wave-lengths are employed.

Fig. 6.



The change in wave-length when X-rays of wave-length 15-17 Å. are scattered by different radiators, showing a smaller change for the heavier elements.

scattered by different elements when hard X-rays are used appears also when hard γ -rays are employed, as is shown in Table II. In this case, however, the difference between the different elements does not become apparent for elements lighter than iron.

I do not feel that these absorption experiments are sufficiently accurate to make from them any reliable estimate of the homogeneity of the scattered X-rays. The spectrum measurements, however, such as those shown in fig. 1, indicate clearly the existence of both a *modified ray*, whose wave-length is changed by the theoretical amount, and an *unmodified ray* of unchanged wave-length. It would seem possible to explain all of the present results on the assumption that only these two rays exist in the scattered beam, but that the energy distribution between the two rays varies with the wave-length, the angle of scattering, and the atomic number of the radiator. According to this view, for short wave-lengths and low atomic numbers nearly all of the energy lies in the modified ray, while for long waves and high atomic numbers the unmodified ray has the greater energy.

These experiments therefore suggest that for such comparatively great wave-lengths as those used in optics, when the usual materials are used as radiators, the unmodified ray should predominate, and the effective change in wave-length due to scattering should be very much less than that which occurs when X-rays are scattered. This is in accord with the negative result of Ross's experiment, in which he attempted to detect a change in wave-length when light was scattered by paraffin.

The Limb-Effect.

If the electrons were really free, which would correspond to atoms of zero atomic number, the present experiments suggest that the change in wave-length predicted by the theory should occur for even very long waves. J. Q. Stewart has recently presented an argument which suggests strongly that there exists about the sun a comparatively dense atmosphere of free electrons*. If this is the case, we should expect, in addition to the spectrum lines transmitted directly through this atmosphere †, to find some scattered light from

* J. Q. Stewart, *Nature*, exi, p. 186 (1923); *Phys. Rev.* xxii. (1923).

† Of course, the solar lines are absorption, rather than emission lines. The change in wave-length should occur, however, in exactly the same manner. For the continuous background on either side of a dark line should be shifted toward the red, which would shift the centre of gravity of the dark line itself.

the atmosphere which would be of greater wave-length than the direct ray. Since the thickness of the atmosphere traversed is greater near the limb, the amount of scattering, and hence the effective increase in wave-length, should be greater at the limb. We might thus expect the mean wave-length of a spectrum line from the sun's limb to be slightly greater than that of the same line from the middle of the photosphere. The difference should probably be less than 0.024 \AA ., since even at the limb the direct ray would probably be responsible for a large part of the spectrum line.

An effect of exactly this character is found in the solar spectrum, and is known as the "limb effect." Dr. C. E. St. John writes me that the wave-lengths from the limb are greater than those from the centre by from 0.004 to about 0.010 \AA . in passing from the violet to the red. This neglects the very strong lines, which show no change in wave-length, and which presumably originate above the denser part of the electron atmosphere. The observed limb effect is thus of the right sign and of the right order of magnitude. At first sight it seems difficult to account for the fact that the red lines are shifted more than the violet. It is very possible, however, that the violet light is the more rapidly absorbed by the sun's atmosphere, so that the violet light reaching us traverses a thinner stratum of electrons. Our ignorance of the relative amount of the primary and the scattered light in the solar lines makes it impossible at present to give this explanation of the limb effect a quantitative test; but qualitatively it seems to be satisfactory.

Possible Origin of the Unmodified Ray.

Two different hypotheses suggest themselves to account for the presence of the unmodified ray. The first is that if the momentum of the light quantum is insufficient to impart to the scattering electron enough kinetic energy to eject it from the atom, the electron is held so firmly that it cannot recoil. Since in this case no energy is lost by recoil, the frequency of the scattered ray is the same as that of the incident ray. According to this view, many of the electrons in the heavier elements would be so tightly bound that they could recoil only from quanta possessing great energy, whereas for low energy or long wave-length quanta, even in the lighter elements some of the electrons would not recoil, thus giving rise to unmodified scattering. This is in accord with experiment. Quantitatively, however, the hypothesis is not so satisfactory. Thus the kinetic energy of an electron

recoiling with the impulse imparted by a molybdenum K α -ray when deflected through 135° is greater than the critical ionizing energy (280 volts) of the K electrons in carbon. We should therefore expect that no unmodified ray should appear when these rays are scattered at 135° by carbon. The spectra exhibited in fig. 1, however, show that the unmodified ray is present under these conditions.

The second hypothesis is based upon the view that when interference occurs, two or more electrons must scatter the same quantum. The theory upon which equation (5) is based, however, supposed that each quantum is scattered by a single electron. The change in wave-length is proportional to $1/m$, where m is the mass of the body which scatters the ray. If, then, the ray is scattered simultaneously by two electrons, the change in wave-length should be $1/2$ the maximum value, and if interference occurs between the rays scattered by a large number of electrons, as in the case of crystal reflexion, the change in wave-length should be negligible. According to the wave-theory, partial interference should always occur when more than one electron is traversed by an electromagnetic wave. Experimentally, however, we have no evidence that the rays scattered by small groups of electrons, such as those in an atom of low atomic number, interfere with each other except when the phases of the rays scattered by the individual electrons are nearly identical. This is the condition, for example, under which excess scattering of X-rays occurs. There is accordingly some justification for the assumption that an electron scatters independently only when removed from other electrons by a distance greater than some fraction of a wave-length of the incident ray. If the electrons are closer than this, they will cooperate in their scattering, and in view of their large total mass, no appreciable change in wave-length will result. This hypothesis therefore leads also to an unmodified ray which possesses greater relative energy as the wave-length of the primary ray and the atomic number of the radiator are increased.

On the latter hypothesis, there should be no change of wave-length when X-rays are regularly reflected from a crystal, or when light is reflected by the free electrons of a metallic mirror, whereas according to the former hypothesis such a change might have been anticipated. The fact that experiment seems not to show any wave-length change in these cases * is a point in favour of the view that the

* The test on light reflected by a mirror has been made by P. A. Ross (*loc. cit.*); that on the wave-length of reflected X-rays is being made in this laboratory.

unmodified ray results from scattering by groups instead of by single electrons.

Summary.

The present absorption measurements on hard X-rays, when combined with the writer's earlier measurements on γ -rays and his spectrum measurements on soft X-rays, show that over the range of primary wave-lengths from 0.7 to 0.024 Å., there occurs a change in wave-length during the scattering process.

For light elements and short wave-lengths the effective wave-length change is very near the theoretical value $\delta\lambda = 0.024 (1 - \cos \theta)$, but is less for long wave-length X-rays and for radiators composed of heavy elements.

It appears probable that in each case the scattered ray consists of two portions, an unmodified ray for which $\delta\lambda = 0$, and a modified ray for which $\delta\lambda = 0.024 (1 - \cos \theta)$. The effective wave-length change then depends upon the distribution of energy between these two rays.

Two different hypotheses are suggested to account for the existence of the unmodified ray.

The limb effect, or difference in wave-length of solar lines between the centre and the limb of the photosphere, receives a satisfactory qualitative explanation on the view that it is due to a change in wave-length as the light is scattered by an electron atmosphere around the sun.

Washington University,
Saint Louis, U.S.A.
June 23, 1923.

XCVI. *The Generalized Quantum Conditions.* By O. W. RICHARDSON, F.R.S., *Wheatstone Professor of Physics in the University of London* *.

FROM a consideration of the equations of motion of an electrified particle on the general theory of relativity, Professor W. Wilson † has suggested an extension of the quantum conditions for such a particle executing a periodic motion, in the form

$$\int (p_s + eA_s) dq_s = n_s h, \quad s = 1, 2, 3, 4. \quad \dots \quad (1)$$

where the p_s and q_s are the Hamiltonian coordinates, e is the

* Communicated by the Author.

† Proc. Roy. Soc. A, vol. cii, p. 478 (1922).

charge, A the four-vector potential, h Planck's constant, and the n_s integral numbers. The integrals in each case are to be extended over the period of the corresponding q . The first three equations are shown to lead to a natural account of the normal Zeeman effect, but the fourth equation is not explicitly considered in the paper. However, about the time at which Professor Wilson read his paper to the Royal Society, he informed me, in conversation, that the fourth equation could be transformed into the quite simple expression

$$-\int (T + V) dt = n_4 h, \quad . \quad . \quad . \quad . \quad (2)$$

where T is the kinetic and V the potential energy of the particle, and t the real time. This equation can readily be verified.

One might be tempted to argue from the symmetry of the equations that n should also be an integer like n_1 , n_2 , and n_3 , but this cannot, in general, be the case, owing to the fact that these numbers are not entirely independent of one another. This may be made clear by considering one or two simple cases.

There are several important types of motion for which the first three members of (1) reduce to the single equation

$$\int p dq = nh, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where n is an integer. If, furthermore, the motions are executed with constant energy (for example, without radiation as in the stationary states of a simple Bohr atom), we have

$$\int p dq = 2 \int T dt, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

So that, for such motions,

$$2 \int T dt = nh, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

In the case of a Planck oscillator

$$\int T dt = \int V dt; \quad . \quad . \quad . \quad . \quad . \quad (6)$$

so that if the motion of a Planck oscillator is to be subject to (3)—or its equivalent (5)—and (2), we must have

$$n_1 = -n. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

In the case of a simple Bohr atom

$$T_n = \frac{1}{2} E e \left(\frac{2}{r} - \frac{1}{a_n} \right), \quad V_n = -E e / r, \quad . \quad . \quad . \quad (8)$$

where the suffix n indicates that the motion referred to is the one governed by the integer n in (3), E and e are the nuclear and electronic charges, r the instantaneous radius, and a_n the semi-major axis. In this formula the potential energy V_n is measured from an infinitely distant configuration. As this is arbitrary, it is perhaps preferable to add an arbitrary constant A to the potential energy. If this is done and equation (2) is to apply to the motion, we have

$$\int \left(A - \frac{Ee}{2a_n} \right) dt = -n_4 h,$$

$$\text{or} \quad Ee/2a_n = n_4 h \omega_n - A,$$

if ω_n is the orbital frequency. Putting in the values of a_n and ω_n required by condition (3), we get

$$2\pi^2 \frac{Mm}{M+m} \frac{E^2 e^2}{n^2 \hbar^2} = \frac{n_4}{n} 4\pi^2 \frac{Mm}{M+m} \frac{E^2 e^2}{n^2 \hbar^2} - A,$$

M and m being the nuclear and electronic masses. This equation shows that A must be zero, otherwise it would depend on n . In order to satisfy the equation, it is necessary and sufficient that

$$n_4 = +n/2. \quad . \quad . \quad . \quad . \quad . \quad (9)$$

We know from the spectroscopic evidence that n can take all integral values; so that for a Bohr atom it appears that n_4 can take positive semi-integral as well as integral values. This result is, however, special to the laws of force governing the motion, because we see from equation (7) that in the case of a Planck oscillator, n_1 is confined to negative integral values.

Provided the velocities in the motions remain small compared with the velocity of light, the results can be generalized to central forces varying as any power of the distance by means of a theorem used by Bohr and Burgers and apparently due to Jacobi*. According to this theorem, if the force varies as r^μ ,

$$\int T dt = \frac{\mu+1}{2} \int V dt. \quad . \quad . \quad . \quad . \quad (10)$$

Using this to eliminate $\int V dt$ from (2), we obtain

$$\int \left(1 + \frac{2}{\mu+1} \right) T dt = -n_4 h,$$

* Cf. Sommerfeld, *Atombau und Spektrallinien*, 3rd Edition, Zusatz (5), p. 666; English translation, p. 548.

which gives, in combination with (5),

$$\frac{n}{2} + \frac{n}{\mu + 1} = -n_4$$

$$\text{or} \quad n_4 = -\frac{\mu + 3}{2(\mu + 1)}n.$$

The following table gives a series of values of n_4 in terms of n for different values of the index μ :—

$\mu \rightarrow$	$+\infty$	$+1$	$+1/2$	0	$-1/2$	-1	$-3/2$
$n_4 \rightarrow$	$-n/2$	$-n$	$-7n/6$	$-3n/2$	$-5n/2$	$\pm\infty$	$+3n/2$
$\mu \rightarrow$	$-5/3$	-2	-3	-4	-5	-6	$-\infty$
$n_4 \rightarrow$	$+n$	$+n/2$	0	$-n/6$	$-n/4$	$-3n/10$	$-n/2$

From this table it will be seen that for a force varying as the direct distance, as in a Planck oscillator, $n_4 = -n_1$; for an inverse square law, as in a simple Bohr atom, $n_4 = +n/2$; for an inverse cube law $n_4 = 0$, and so on. Whilst the physical interpretation of these numerical connexions is not yet clear, the occurrence of the factor $1/2$ with the inverse square law seems suggestive in relation to the fact that the individual constituents of band spectra require half-quantum numbers for their series arrangements. It also seems possible that the fractional relations arising with the more unusual laws of force may be connected with the complex Zeeman effects which appear to be symptomatic of motions in intra-atomic fields of complicated types.

The integrals expressed in this paper are to be read as definite integrals extended over a complete period of the relevant q (or t).

April 1923.

Note added Sept. 2, 1923.—It may be objected that since $T+V$ is constant in the motions considered there is no mathematical periodicity in time of this function. There is, however, a periodicity in the physical properties of the energy. An alternative procedure suggested by W. Wilson would be to use the fourth relation to define an additional frequency.

XCVII. *The Relative Activities of Radioactive Substances in an Unchanged Primary Uranium Mineral.* By W. P. WIDDOWSON, B.A., Scholar of Christ Church, Oxford, and A. S. RUSSELL, M.A., D.Sc.*

§ 1. *Introduction.*

THE work of Boltwood † showed that in an unchanged primary uranium mineral there are about 2.2 atoms of uranium breaking up per second for one of each of its disintegration products, and that the total activity due to the actinium series is about 0.28 of that of uranium taken as unity. From this it was deduced that uranium consists of two radio-elements, Uranium I and Uranium II, in equilibrium, and the scheme to give these a place in the radioactive series, suggested by one of us ‡ was confirmed later by the experimental work of Fajans and Göhring §. To account for the 0.2 in excess of 2, Rutherford ¶ suggested that branching occurred either at Uranium I or Uranium II, one of these elements undergoing a dual change with the expulsion of an α -particle, forming two products which give rise to the uranium and actinium series respectively. Rutherford suggested that 8 per cent. of the parent substance was transformed into the actinium series; but it may also be calculated from Boltwood's results that if the change occurs at uranium I 26 per cent. breaks up, and if at uranium II 14 per cent. to form the actinium series. Later experiments, however, notably those of Hahn and Meitner ¶¶, showed that the actinium series had only 3 per cent. of the activity of the radium series, and Meyer ** found it to be 4.2 per cent. The discrepancy is striking, and one of the objects of this work was to elucidate this point.

The relative activities of certain radio-elements of the uranium series and of the whole actinium series when in equilibrium have been evaluated from the calculated relative ionizations of the α -ray bodies on various assumptions respecting the amount and the place of branching. These are given in Table I. This table includes also calculations

* Communicated by the Authors.

† E. B. Boltwood, *Amer. Journ. Sci.* vol. xxv. p. 269 (1908).

‡ A. S. Russell, *Chem. News*, vol. cvii. p. 49 (1913).

§ K. Fajans and O. Göhring, *Phys. Zeit.* vol. xiv. p. 877 (1913).

¶ Sir E. Rutherford, 'Radioactive Transformations,' p. 170 (1906).

¶¶ O. Hahn and L. Meitner, *Phys. Zeit.* vol. xx. p. 529 (1919).

** S. Meyer, *Wien. Anzeiger*, p. 133 (1920).

made on the assumption that actinium arises from an isotope of uranium of atomic weight 239, whose activity is either 3 or 8 per cent. of that of uranium I. The calculated values are compared with those obtained by Boltwood † in his original paper, and with those given by Johnstone and Boltwood ‡ in a subsequent paper, which substantially confirm the earlier one. The latter are marked with an *.

TABLE I.

No branch in the Uranium series.	Branch at Uranium I.		Branch at Uranium II.		Independent isotope parent of Ac. series.		Boltwood's values.
	3 %.	8 %.	3 %.	8 %.	3 %.	8 %.	
Whole mineral Uranium 5.23	5.31	5.47	5.24	5.26	5.25	5.29	4.64, 4.73 *
Ionium Uranium 0.56	0.55	0.54	0.54	0.52	0.55	0.52	0.34
Radium Uranium 0.60	0.59	0.57	0.58	0.55	0.58	0.55	0.45, 0.49 *
Polonium Uranium 0.65	0.64	0.62	0.63	0.60	0.63	0.60	0.46
Actinium Series Uranium ...	0.145	0.39	0.143	0.38	0.17	0.42	0.28

It is seen from this table that the effect of branching in the series is, as one would expect, to alter the ratio of uranium to one of the products in the major branch, but to have a small effect only on the ratio of uranium to the total activity of the whole mineral. (This is explained by the fact that the number of ions produced by single α -particles from the products of the actinium series is nearly equal to that produced by single α -particles from the products of the uranium series.) Boltwood's work appears to show that *both* of these ratios are abnormal; in other words, although the assumption that branching occurs explains the lowness of such ratios as ionium to uranium, polonium to uranium, etc., it does not explain that of the whole mineral to uranium. To explain both it would appear simplest to assume in addition that the

† B. B. Boltwood, *loc. cit.*

‡ J. H. L. Johnstone and B. B. Boltwood, *Phil. Mag.* vol. xl. p. 50 (1920).

uranium used by Boltwood is more active than is to be expected. This might be explained by one of the following reasons:—

- (1) The α -particles from uranium ionized relatively more than is to be expected from their range in the electro-scope used.
- (2) An α -ray body not of atomic number 92 was present in his uranium.
- (3) An isotope of uranium is present which emits α -rays, and initiates a disintegration series which is not completed like the radium and actinium series.
- (4) A branch series of considerable magnitude begins at radium (which is known to emit β -particles as well as α -particles).

It cannot be argued that Boltwood failed to make quantitative separations of the individual products, because the aggregate of their separate activities is approximately that of the mineral before separation.

Of the possibilities enumerated, (1) is unlikely, (2) out of the question, (3) is possible but there is no proof at present that it is true, (4) has been definitely disposed of by Hahn and Meitner*.

In order to throw light upon the subject, if possible, we have carefully repeated part of Boltwood's work, using the improved chemical methods that have been developed since 1906. The results obtained will now be described.

§ 2. *Methods of making Measurements.*

The α -ray electro-scope used in these experiments had an ionization chamber of 10.3 cm. in diameter and 13 cm. in height. A disk of brass was attached by the rod to the gold-leaf system, and fixed so as to be in a plane parallel to that of the disk of radioactive matter, at a distance of 6 cm., the disk being carried on the removable base. This allowed the rays to give complete ionization; and the rate of collapse of the gold-leaf (after being charged to about 700 volts in the usual way, which is sufficient to give the saturation current) was found by timing the fall over a certain number of divisions on a scale in the eyepiece of a reading-microscope.

The sensitiveness of the instrument was such that 1 milligram of radioactively-pure uranium oxide (U_3O_8) gave a net leak of 0.83 division per minute. The natural leak

* O. Hahn and L. Meitner, *Zeit. Physik*, vol. ii. p. 60 (1920).

was about 0.78 division per minute, and was very constant, never varying beyond 0.02 or 0.03 division per minute throughout the research.

The radioactive matter was contained on copper disks 3 cm. in diameter, which for convenience of handling were supported on small stands. Films were made by grinding the substance to be measured to a very fine powder, making it into a suspension in chloroform, and painting this evenly on to a copper disk in the way recommended by McCoy. When the chloroform evaporated, an even film was left which adhered to the disk so that it could be moved about without fear of loss.

The chief difficulty in making comparative measurements of activity by measuring the ionization due to α -rays is the great absorption of these rays by the material containing the active matter. This is so great that with increasing thicknesses of film a limit is reached beyond which there is no further increase of activity due to α -particles.

There are three ways in general use for getting over this difficulty, each of which has disadvantages. (1) McCoy * takes weighed films of increasing thickness and measures their activities, plots the weight against the ratio of weight to activity, and extrapolates his curve to obtain this ratio at zero weight, *i. e.* for a very thin film in which there is presumably no absorption. (2) Seddy uses the "limiting activity" method. In this method films are made of such thickness that their activity has reached its maximum. The product of the weight and the activity of such a film bears a simple relation to the activity obtained by the other methods. (3) Boltwood † and others advocate using films made of very small quantities of material. In such films the absorption is small, and for comparative measurements on similar films may be neglected. It is understood, of course, that whatever method be employed disks of one diameter only must be used throughout the series of measurements.

We employed the method (1) at first, but our experience after making many careful measurements is that it was difficult to get the good curves obtained by McCoy, and that it was not possible by extrapolation to obtain a very certain zero result. With it we obtained results for the activities of ionium, uranium, and for the whole ore which appeared to be of the right order; but we abandoned it later for method (3), which we think is the best.

In method (2) a comparatively large quantity of material

* H. N. McCoy, *Phil. Mag.* vol. xi. p. 176 (1906).

† B. B. Boltwood, *Amer. Journ. Sci.* vol. xxv. p. 269 (1908).

is required. For the disks we used, about 100 mgs. of material was required to give maximum activity. This has the disadvantage that it is not always possible or desirable to obtain this amount of material. Nor is it possible to compare directly a very thin film, such as is obtained when polonium is deposited electrolytically, with a film of this kind.

The third method was the one eventually adopted in these experiments. Films, which were never allowed to exceed 5 mgs. in weight, were made as described above, and it was assumed in these circumstances that there was no absorption. The great drawback to this method is the accurate determination of the weight of the films. In practice the disk was weighed just before the film was applied and, to check it, just after its removal, and if there was any difference the mean of the two readings was taken. A balance was used which made it possible to weigh to the twentieth of a milligram. It was found that fairly consistent results were obtained, as is shown by the following figures :—

Weight in mgs.	Activity (div./min.).	Activity per mg.
4.50	6.60	1.47
3.95	5.86	1.485
4.75	6.93	1.46
2.70	4.01	1.49

For convenience, activities in divisions per minute will be referred to hereafter simply as activities.

§ 3. *Purification and Activity of Uranium Oxide (U_3O_8).*

It is essential for this work to know accurately the activity of a specimen of uranium oxide (U_3O_8), pure chemically and free from all radio-elements except its own quick-changing β -ray products, uranium X_1 , uranium X_2 , uranium Y , and uranium Z . This was obtained by the following standard procedure.

To a solution in water of a few grams of uranium nitrate, a solution containing a few milligrams of lead and bismuth nitrates was added, and hydrogen sulphide passed through the acidified solution, the precipitated sulphides being filtered off and the solution boiled. The precipitate contains proto-actinium and all the disintegration products after the radium emanation which might be present. A solution containing a few milligrams of thorium nitrate

was added to the filtrate, and the thorium precipitated from nearly neutral solution by hydrofluoric acid. This removes products of atomic numbers 90 and 89. The filtrate was boiled to expel hydrogen fluoride completely. To it was added a solution containing a few milligrams of barium chloride. The barium, precipitated by dilute sulphuric acid, carries with it products of atomic number 88.

The uranium was then precipitated with ammonia and dissolved in ammonium carbonate, filtered, the precipitate treated with nitric acid, the carbon dioxide expelled, and the uranium again precipitated with ammonia. This was repeated three times, and the yellow ammonium uranate so obtained was ignited in a crucible to uranium oxide (U_3O_8), with which the films were made.

The original uranium salt was probably comparatively free from radioactive impurities, the above treatment making it quite so, except of course for the quick-changing products which soon grow again. The effect of the β -particles from these in the electroscope was just less than 2 per cent.

Its purity with regard to its formula, U_3O_8 , was tested by dissolving in sulphuric acid and reducing it quantitatively by zinc amalgam, and titrating the uranous solution with N/20 permanganate solution.

A specimen of purified U_3O_8 lent to us by Prof. F. Soddy gave a very similar activity to our own.

A disk of this material was kept as a standard, and measured from time to time to ensure that the sensitiveness of the gold-leaf did not change during the course of the research. The extreme difference found was 0.14 div. in 17 div., which is less than 0.9 per cent.

The following results for U_3O_8 were obtained:—

Weight (mgs.).	Activity.	Activity per mg.
3.25	2.74	0.845
3.55	3.02	0.852
3.15	2.60	0.827
3.275	2.66	0.812

These results give a mean activity of 0.834 per mg. Therefore 1 gram of an ore containing 38.4 per cent. U_3O_8 will have an activity 320. It was found that 2 per cent. of this was due to the ionization of uranium X and uranium Y. The corrected activity is therefore **313.5**.

§ 4. *The Analysis and Activity of Pitchblende.*

The pitchblende used throughout these experiments consisted of lumps of mineral about the size of peas, which were ground up to a very fine powder. It was analysed by dissolving about half a gram in dilute nitric acid, removing the silica by filtration, the lead as sulphate, and the iron as ferric hydroxide in presence of excess of ammonium carbonate; the uranium was finally precipitated as ammonium uranate from a solution freed from carbon dioxide and estimated as U_3O_8 in the usual way. A mean value of 38.4 per cent. U_3O_8 was obtained from three experiments. This was checked (*a*) by estimating uranium volumetrically after the removal of iron, and (*b*) by the radium-emanation method against a carefully analysed specimen of a primary thorianite.

The following results were obtained from films of the material on the day the films were made:—

Weight (mgs.).	Activity.	Activity per mg.
4.50	6.60	1.47
3.925	5.86	1.49
4.75	6.93	1.46
2.70	4.01	1.49

The mean activity of 1.48 per mg. was found to increase, as though there had been a temporary loss of emanation in the making of the films. A fortnight later the mean activity per mg. was found to be 1.545, which did not increase further. The films were then assumed to be in the position that any loss of activity due to diffusion of emanation from them was constant. This permanent loss of emanation, due to the finely-ground state of the ore, was corrected for in the usual way. Emanation was completely expelled from an untouched portion of the finely-ground material, and its amount measured in the usual way in an emanation electroscope. The solution was sealed up for a known time, and from the quantity which had in that time been formed the total amount in equilibrium was calculated. This was found to be 4 per cent. greater than the first. 4 per cent. is consequently the amount of emanation permanently lost by diffusion. In addition to radon, radium A and radium C' alone are affected. The correction to be applied to the mineral is therefore calculated to be 1.8 per cent. The corrected activity per gram of ore is in consequence 1573. There was no trace of thorium in the mineral.

§ 5. *Estimation and Activity of Polonium.*

Polonium may be estimated in two ways:—

- (a) By deposition from solution on to a copper disk;
- (b) By chemical separation with bismuth.

The first was obviously, and was also found by experiment to be, the better way. In this method about 0.6 gram of pitchblende was digested with strong hydrochloric acid and filtered from undissolved silica. The solution, which was somewhat neutralized, was made up to 150 c.c., and in it a copper disk was rotated just below the surface, by an electric motor. The disk was attached to a rotating glass rod by means of Bunsen cement, which allowed it to be removed easily after the experiment. One face of the disk was highly polished, the remainder of it being coated with paraffin wax. After one and a half hours the disk was removed and a second substituted for it. This was again replaced after a similar interval, and so on till all the polonium was deposited as infinitely thin films whose activity was determined in the electroscope. This was found to take about nine hours.

The decay of these films was followed in the electroscope, and assuming the half-value period to be 136 days, the amount at the beginning was calculated back and the mean of the values taken. No readings were taken till after the first day, so as to allow any quick-changing bodies deposited to decay.

In an experiment in which the ore was taken up with sulphuric acid, no activity at all could be obtained on the disks.

Owing to the great tendency of polonium to deposit itself from solution, as shown by Boltwood, these experiments were always carried out immediately after the ore was dissolved.

First Experiment.

The polonium was derived from 0.6436 gm. of ore.

Activity after	1	5	9	33	54 days.
	133.4	128.7	125.7	110.9	101.8
Initial activity calculated } back to zero	134.1	132.0	131.6	131.2	134.0

Giving mean of 132.6.

Activity per gram of ore is 204.

Second Experiment.

The polonium was derived from 6276 gm. of ore.

Activity after	1	27	46 days.
	120.7	106.4	97.8
Calculated back to start...	121.3	122.0	123.7

Giving mean of 122.3.

Activity per gram of ore is 195.

From the above figures a value of 200 was taken as the activity due to polonium.

§ 6. *Estimation and Activity of Radium.*

The activity in the mineral due to radium was estimated by precipitating it along with barium as sulphate. To a solution of the ore in hydrochloric acid, a few drops of bismuth and thorium nitrates were added and sufficient barium chloride solution to give about 100 mgs. of the sulphate. The hydroxides of uranium, bismuth, thorium, etc. were precipitated with ammonia and filtered off. This precipitate was dissolved up and reprecipitated so that any adsorbed barium chloride in the first precipitate remains in solution the second time. The ammoniacal solutions were added together and made just acid with hydrochloric acid, excess of sulphuric acid added, and the resulting barium sulphate collected, dried, weighed, and its activity determined on disks in the usual way.

It was found that the films so made gained 27 per cent. in activity in 16 hours. In order, therefore, to avoid as far as possible disturbances due to the growth of the emanation and its products in the radium, this procedure was improved so that readings might be made in a minimum time after the precipitation.

It was assumed for this purpose that when a certain amount of barium is added to a solution containing radium, the latter behaves exactly like the former in the few chemical operations through which they are put: so that if, say, 90 per cent. only of the barium present is precipitated, exactly 90 per cent. of the radium is precipitated with it. Accordingly, to the solution of the ore a known weight of barium chloride was added, and hence the corresponding weight of sulphate could be calculated. In practice 10 c.c. of a solution containing 3.978 gs. of hydrated barium chloride per 250 c.c., that is 159 mgs. in the 10 c.c., which is equivalent to 152 mgs. of the sulphate. The experiment was

then conducted as before, except that it was not necessary to reprecipitate the hydroxides, and the precipitate of barium sulphate when formed was filtered as quickly as possible at the pump, the filter paper was immediately ignited, the films made and their activity at once measured. The films were weighed later, and from their weight and activity it was calculated how much activity there was in the 152 mgs. barium sulphate, *i. e.* in the quantity of mineral taken.

In these experiments nitric acid was found to be unsatisfactory as a solvent for the mineral, because the latter contains sulphur which was oxidized by the nitric acid to give sulphate, and this of course immediately precipitated a certain amount of the barium on addition. With hydrochloric acid this difficulty did not arise, and for this specimen of pitchblende it was found to be as good a solvent as nitric acid.

First Experiment.

Weight of ore, 1.713 gm.

Weight of barium sulphate, 0.152 gm.

Weight (mgs.).	Activity.	Activity per mg,
4.075	8.95	2.20
3.375	7.51	2.22
3.85	9.05	2.35

As a mean, 1 mg. had an activity of 2.25 : therefore
152 mgs. had 342.

Activity of 1 gm. of ore is $\frac{342}{1.713}$, *i. e.* 200.

Second Experiment.

Weight of ore, 1.1626 gm.

Weight of barium sulphate, 0.152 gm.

Weight (mgs.).	Activity.	Activity per mg.
3.95	6.17	1.56
2.30	3.68	1.60
3.70	5.32	1.44

As a mean, 1 mg. had an activity of 1.53 : therefore
152 mgs. had 232.5.

Activity of 1 gm. of ore is $\frac{232.5}{1.1626}$, *i. e.* 200.

There is a small correction (about 4 per cent.) because of the presence of actinium X.

The mean activity per gram of ore is therefore 192.

§ 7. Estimation and Activity of Ionium.

The method used for separating ionium was essentially that described by Marckwald and Russell*, which consists in adding a few milligrams of a soluble thorium salt to a solution of 1 g. of the mineral, separating the thorium quantitatively as fluoride by means of potassium fluoride, converting the fluoride into oxide by ignition, fusing the oxide with potassium hydrogen sulphate, dissolving the melt in hot water, and precipitating the thorium as hydroxide. The thorium is next freed from bodies of atomic weight 89 by one of the standard procedures. Finally the thorium is obtained in dilute sulphuric acid and then made up to 50 c.c., and aliquot parts of this solution carefully evaporated down on a copper disk on a hot plate, care being taken to get as even a film as possible.

There was fair agreement between the activities of the different disks containing the same amount of material, as the following results show :—

Weight of ore, 0.534 gs. Solution of thoria made up to 50 c.c.

5 c.c.	gave an activity of	9.61
2 c.c.	„ „	3.82
2 c.c.	„ „	3.84

Therefore as a mean 50 c.c. has an activity of 95.9, and
 1 gm. of ore $\frac{95.9}{0.534}$, i.e. 180.

A blank test shows that the ionization due to the thorium itself was negligible. The ionization due to the radioactinium was estimated as 4 per cent. of that of ionium from the known amount of radioactinium present and the number of ions each α -particle from it produces. The activity of ionium is consequently 173.

§ 8. Estimation and Activity of Proto-actinium.

6.00 gs. of the pitchblende were boiled vigorously in dilute nitric acid for an hour. The residue, after filtering, was dried and found to be active. A few milligrams of tantalum oxide were added to it and the whole fused with potassium hydroxide in a nickel crucible. The melt was dissolved in cold water, and the unattacked residue was found to be inactive. It was presumed that the whole

* W. Marckwald and A. S. Russell, *Jahr. d. Radioakt.* vol. viii. p. 45 (1911).

of the tantalum remained in solution, together with the whole of the proto-actinium which had been in the first residue. This alkaline solution was added to the original acid filtrate, and after neutralizing with ammonia and adding a little dilute sulphuric acid the solution was boiled vigorously for fifteen minutes, on which the tantalum settled out, presumably quantitatively, in a flaky condition which was easily filtered*. In order to free the active tantalum from radio-elements other than those of atomic number 91, it was fused with potassium hydrogen sulphate and the melt dissolved in hot water. The tantalum alone was found to be thrown out of solution. Radio-elements other than those of atomic number 91 present remained in solution. The tantalum was filtered off and the operation of fusing repeated. Finally the tantalum was ignited and weighed, the activity being measured in the form of a film in the usual way.

It follows from the chemical operations that the only active radio-element present with the tantalum after uranium X_2 had decayed away was proto-actinium.

Weight of ore, 6.00 gm.

Weight of tantalum oxide, 0.011 gm.

3.0 mgs. gave an activity of 8.40

5.2 mgs. „ „ 14.28

Therefore as a mean 11 mgs. has an activity of 30.47,
and 1 gm. of ore $\frac{30.47}{6.00}$, i. e. 5.08.

§ 9. Discussion of Results.

Table II. below includes the results of this research in column two. In the third column are given the numbers of ions produced per α -particle when one is emitted, or per average α -particle when more than one is expelled. These have been calculated from the ranges of the α -particles. The fourth column contains the relative number of atoms of the different substances in equilibrium breaking up per second, and is calculated from the experimental results. The results for polonium might appear best to be used as a standard for comparison, as this element is easily separated quantitatively and its α -particles are practically unabsorbed when it is in the form of a film. Ionium, however, has been chosen

* W. G. Guy and A. S. Russell, Journ. Chem. Soc. (1923), in the press.

because its films resemble in thickness and method of preparation those of all the other substances except polonium, and it is capable of being separated quantitatively.

TABLE II.

Substance.	Activity.	No. of ions per α -particle $\times 10^{-3}$.	Relative No. of atoms breaking up per second.
Pitchblende	1573	1.59	7.82
Uranium	313.5	1.22	2.04
Ionium	173	1.37	(1.00)
Radium.....	192	1.45	1.05
Polonium ..	200	1.58	1.00
Proto-actinium.....	5.1	1.41	.029

The table shows that

- (a) The relative activity of proto-actinium in the ore is nearly 3 per cent.
- (b) The relative activity of uranium is only about 2 per cent. greater than is to be ascribed to the expulsion of two α -particles. If (a) be correct, the value in the fourth column should be 2.06.
- (c) Although the activity of radium is unexpectedly high, the results for ionium, radium, and polonium agree as well as might be expected considering the experimental difficulties and the uncertainty of the correction for relative ionization per α -particle.
- (d) The value in the fourth column for pitchblende is low. Theoretically it should be 8 plus small percentages due to the ionization produced by the β -particles from the radio-elements in the ore, and by the α -particles from the ultimate parent of the actinium series.

The results are also given in Table III. They are there compared with the calculated values of Table I. Values of the ratio proto-actinium to uranium are substituted for those of the ratio actinium series to uranium.

TABLE III.

	No branch in the Uranium series.	Branch at Uranium I.		Branch at Uranium II.		Independent isotope parent of Ac. series.		Results obtained in this research.
		3 %.	8 %.	3 %.	8 %.	3 %.	8 %.	
Whole mineral Uranium	5.23	5.31	5.47	5.24	5.26	5.25	5.29	5.00
Ionium Uranium	0.56	0.55	0.54	0.54	0.52	0.55	0.52	0.55
Radium Uranium	0.60	0.59	0.57	0.58	0.55	0.58	0.55	0.61
Polonium Uranium	0.65	0.64	0.61	0.63	0.60	0.63	0.60	0.64
Proto-actinium Uranium	0.015	0.0405	0.015	0.0395	0.018	0.0435	0.016

It is seen from this table that, while there is no difficulty in deciding that the actinium series forms about 3 per cent. of the uranium series, it is not possible with the results obtained to decide whether actinium comes from a branching in the uranium series at uranium I or uranium II, or from an independent isotope. It would appear that this point can only be settled experimentally by a determination of the atomic weight of proto-actinium, and the definite proof or disproof, by Aston's method, of the existence of an isotope of uranium genetically independent of uranium I.

The results disagree with those of Boltwood in

- (a) The relative activities of polonium, ionium, and radium to uranium. His are much lower than those obtained, which are those normally to be expected.
- (b) In the ratio of uranium to one of its disintegration-products corrected for the relative ionization of these bodies, 2.04 against his 2.2.
- (c) In the ratio of the amount of the actinium series to that of the radium, 2.9 per cent. against the 8 per cent. deduced by Rutherford from his results.

On the other hand, we appear to agree with Boltwood that the ratio of the activity of the whole mineral to that of uranium is lower than is to be expected, his experimental value being 11 per cent. lower than the calculated value, ours 5 per cent. We are inclined to think that there is nothing of importance in this low result, and that it may be satisfactorily explained on two grounds:—(1) Our

assumption that there was no absorption of α -particles by the material composing the films measured was possibly less true of the pitchblende films than of the others; and (2) the dimensions of our electroscope possibly prevented the long-range α -particles from radium C' from ionizing to their fullest extent.

The result obtained for the activity of the actinium series referred to that of the radium series (the branching factor, if branching occurs) 0.029, agrees with the value of Hahn and Meitner*, 0.03 \pm 0.003, and is lower than Meyer's†, 0.042. The result is also consistent with the experimental values of the ratio of the relative activities of uranium Y and uranium X. This ratio should be equal to the above ratio if uranium Y is connected genetically with the actinium series, but it cannot be accurately interpreted owing to uncertainty concerning the relative ionization of β -particles of different penetrating power. Hahn‡ found 0.021; Kirsch§, at most, 0.042; Guy and Russell|| 0.032.

SUMMARY.

1. The work of Boltwood on the relative activities of the radioactive constituents of a uranium mineral has been carefully repeated. Our results agree with his on the lowness of the relative activity of the mineral to that of the uranium it contains, but disagree on the relative activities of polonium, ionium, radium, and uranium. For these we find values close to those expected by theory.

2. We find the ratio of the activity of the actinium series to that of the radium series to be 0.029, in agreement with Hahn, but in disagreement with the value 0.08 deduced by Rutherford from Boltwood's results, and with the value 0.04 obtained experimentally by Meyer.

3. It is concluded that measurements along the lines of those in this paper cannot decide whether the actinium series arises as a branch of the uranium series or comes independently from an isotope of uranium.

The authors wish to thank the Government Grant Committee of the Royal Society for materials and apparatus used in this work.

Dr. Lee's Laboratory,
Christ Church, Oxford.
July 1923.

* O. Hahn and L. Meitner, *Phys. Zeit.* vol. xx. p. 529 (1919).

† S. Meyer, *Wien. Anzeiger*, 133. (1920).

‡ O. Hahn, *Phys. Zeit.* vol. xiv. p. 203 (1914).

§ G. Kirsch, *Wien. Ber.* vol. cxxix. 2 a, p. 309 (1920).

|| W. G. Guy and A. S. Russell (*loc. cit.*).

XCVIII. *Partitioning of Space into Enantiomorphous Polyhedra.* By W. BARLOW, F.R.S. *

An Exhaustive Partitioning into Similar Plane-faced Cells of two Enantiomorphous Forms equally numerous. The cells formed have 13 faces and the unlimited system produced presents Hemihedral Cubic Symmetry.

IN 1894 the author directed attention to the partitioning of space without remainder into similar cells all of the same pattern, but presenting more than one orientation †; and in 1914 he indicated the possibility of a partitioning into space-filling similar polyhedral cells each having 13 plane faces ‡.

A method for achieving such a partitioning will now be described.

CONSTRUCTION.

1. Draw three sets of parallel equidistant planes in three directions mutually at right angles so as to divide space into equal cubes.

2. Construct a cubic system of non-intersecting trigonal axes by drawing endless lines in the four directions of the body-diagonals of the cubes so that every cube is transfixcd by a single diagonal only, while none of the lines thus drawn intersect: one fourth of the total number of endless cube diagonals possible are thus drawn. But one kind of arrangement is producible by the prescribed process §.

3. Select one half of the cubes symmetrically and so that each cube of the selected set has contact at edges only with other selected cubes; this set has face-contact with cubes belonging to the identical complementary set.

4. In each cube of a set thus selected find two points lying on the single diagonal drawn, equidistant from the cube centre and so situated that the distance apart of the two points equals the distance separating nearest points not on the same diagonal in the unlimited point-system consisting of all the points. A single individual cube of

* Communicated by the Author. Appears also in the *Zeitschrift für Kristallographie*, Bd. lviii. pp. 605-628.

† Groth's *Zeitschr. f. Kristallogr.* xxiii. pp. 38, 59, 60, Tafel II. figs. 13, 16, 17, 18; and xxv. p. 1.

‡ Proc. Roy. Soc. London, A. vol. xci. p. 1 (1914).

§ Groth's *Zeitschr. f. Kristallogr.* xxiii. pp. 7-9.

each set is represented in figs. 1 a & 1 b. Slender wooden rods are employed to outline each skeleton cube and to supply it with a single diagonal stay which occupies the

Fig. 1 a.

Fig. 1 b.

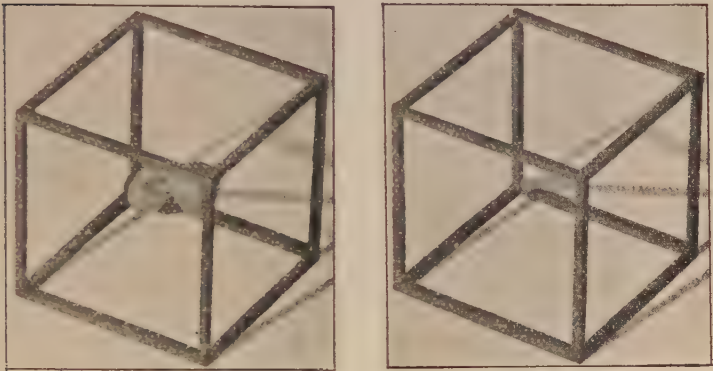
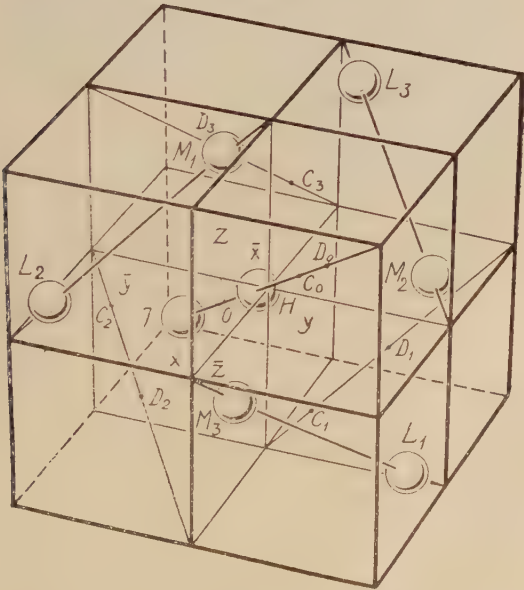


Fig. 2.



position of the diagonal selected as trigonal axis. The two points found are indicated as centres of the small spheres transfixes by this diagonal. Fig. 2 gives a compact group

of 8 skeleton cubes forming a composite space-unit from which the unlimited system is developable by means of translations. The coincidence operations of the unlimited double-point-system formed of all the points are of type 1 a_1 in Barlow's list, centres of symmetry consisting of two kinds being present at all the centres of the cubic cells of both sets*.

The fundamental point-system consists entirely of singular points †, and has the following properties:—

- (a) Each point lies on some trigonal axis of rotation of the unlimited system.
- (b) It is by hypothesis equidistant from the second point on this axis present in the same cell and from some other nearest points lying on other axes in other cells.
- (c) These other points are six in number, making therefore seven points equidistant from the given point. For of the 12 cubic cells with which the cell of the selected point has contact at its twelve edges, 6 are nearer to the selected point than are the remaining 6, and the former six alone furnish points equidistant with the second point in the diagonal from the selected point.
- (d) Reasoning similar to the above establishes the existence of six *next nearest* points, at slightly greater distance, equidistant from each point. These, with the seven points of (c), constitute a group of 13 points immediately surrounding every point of the point-system.

5. Next join every point with each of the 13 points thus immediately surrounding it, and through the points of bisection of these joining lines draw planes each perpendicular to its line and of such extent as to meet, but not intersect, contiguous planes thus drawn. The system of similar plane-faced cells thus produced is that required.

In consequence of the symmetry of the system the planes drawn as prescribed enclose no spaces other than these similar cells which are, as will be shown, enantiomorphous polyhedra each having 13 faces: the two enantiomorphous kinds of cell are equally numerous and similarly distributed. Fig. 3 shows a pair of the cells, one of each kind, having one face which is a regular hexagon in

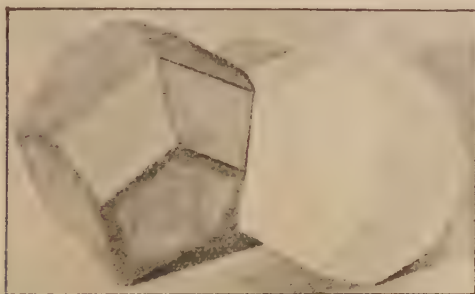
* Groth's *Zeitschr. f. Kristallogr.* xxiii. pp. 43 & 44.

† *Ibid.* p. 60, where a general definition of a system of singular points is given.

common: the centre of this face is a centre of symmetry. The form of cell and its properties are traced as follows*.

As a result of the presence of the trigonal axes and of centres of symmetry which lie on these axes, an interface drawn to bisect a line joining two nearest points both on the same axis, namely through a centre of symmetry situated at the point of bisection, is, as just stated, a regular hexagon. Each angular point of this hexagon is common to two enantiomorphously-related cells separated by the hexagonal interface (see fig. 3); also to two other

Fig. 3.



cells, the axes of which are differently oriented and neither of them parallel to that common to the pair connected by the interface. Thus each angular point of a hexagonal interface is common to four cells.

Within each of the complementary set of skeleton cubes, which do not contain any point of the fundamental point-system, the combined operation of the centre of symmetry at the centre of this cube and the trigonal axis on which this centre lies, produces, as at the centres of symmetry just dealt with, a sixfold repetition; but here the centre of symmetry is a point common to six of the polyhedral cells. And the trigonal axis passing through it forms the common edge of each of two triangularly-arranged sets of three cells, the three individuals of a set being in each case related by this trigonal axis, and the one set being developable from the other by an operation about the centre of symmetry just referred to.

The less regular 12 faces of a cell, which, with the

* The arguments employed will be more readily followed with the aid of a set of skeleton cubes and a few cardboard cells constructed with the aid of the *net* given by fig. 10 below.

hexagonal face, make up the 13, fall into four groups each comprising three similar faces related by coincidence operations about the trigonal axis which passes perpendicular to the hexagonal face of the cell through its centre. The four groups display however but two distinct forms of face, the one quadrilateral the other irregular-pentagonal; but in both cases, notwithstanding identical relation to the system as a whole, two sets of three faces of each form are distinguishable on a single cell, one set bearing a different relation to this cell from that borne by the other.

A polyhedron has 19 solid angles, namely : 6 triads each consisting of three similar solid-angles equals 18, and one making the 19th through which the trigonal axis of the cell passes. The solid-angles forming a triad are, in each case, related by this trigonal axis.

As a means of locating the angular points of a polyhedron with respect to its axes and to the centre of symmetry at the middle of its hexagonal face, there are the following properties traceable on examination of the group of skeleton cubes employed :—

Each of the angular points of the polyhedron is the centre of a sphere circumscribable about a tetrahedron formed by joining some four neighbouring points of the original point-system. And in three cases the sphere passes through two more of these points, thus circumscribing an octahedron outlined by lines forming six points.

These properties are established as follows :—

Each angular point of the polyhedron is, by the construction employed, the point of intersection of at least 3 plane faces each drawn to bisect at right angles one of three lines drawn from some point of the point-system to three neighbouring points of this system. By joining the extremities of the three lines a tetrahedron is completed the centre of the circumscribing sphere of which is the point of intersection of the 3 planes.

Again, those of the cubic units which do not contain any points of the point-system are each in face-contact with six of the units containing points and are similarly related to six nearest points of this system. Consequently the centre of symmetry found in every such unit is the point of meeting of and similarly related to six polyhedra, owing to the operation of the centre of symmetry and the trigonal axis which passes through it. Further, a sphere can be circumscribed about the symmetrical octahedron produced by joining the six nearest points referred to.

The complete form and relative dimensions of a single cell are arrived at by the following steps:—

- A. Find the coordinates of any selected point of the point-system and of the 13 points of the system immediately surrounding it, as referred to axes parallel to edges of the cubic cells, the origin being at the centre of symmetry lying midway between the selected point and that nearest point of the 13 which lies on the same trigonal axis: namely, at the centre of the cubic element containing those two points. The edge of a cubic cell is taken as unit.
- B. Find the coordinates of the points of intersection of the planes drawn as prescribed to form a single polyhedral cell.
- C. Find the lengths of the various edges of a cell.
- D. Find the shapes of the plane faces of a cell.
- E. Construct a "net" showing these faces as they would be related if, while remaining attached at single edges, they were hinged and spread out in the same plane.

A.

For finding the coordinates of a selected point and the 13 points immediately surrounding it.

The distance of each point from the centre of the cube within which it lies being the same and, by hypothesis, such that the distance apart of nearest points on the same axis is equal to that between nearest points not thus related, the value n of the distance of a point from the nearest corner of its cubic cell is readily obtainable. Thus, taking the edge of a cubic element as unity, the distance separating two nearest points on the same axis is $\sqrt{3}-2n$, and since two nearest points not thus related lie in a plane which is parallel to one of the three sets of cube faces, and a line drawn in this plane equidistant from the two points, parallel to a cube edge, is at a distance $\frac{n}{\sqrt{3}}$ from each of them,

it follows that the distance apart of the two points is $\sqrt{1+\left(\frac{2n}{\sqrt{3}}\right)^2}$. And thus by hypothesis

$$\sqrt{3}-2n = \sqrt{1+\left(\frac{2n}{\sqrt{3}}\right)^2}$$

and

$$n = \frac{\sqrt{3}}{4}(3-\sqrt{5}) = \cdot 33082.$$

Further $2r$, the distance apart of nearest points,

$$= \sqrt{3} - 2n = 1.73205 - .66164 = 1.07041.$$

And the distance between next nearest points $2s$

$$\begin{aligned} &= \sqrt{(2r)^2 + \left(1 - \frac{2n}{\sqrt{3}}\right)^2} \\ &= \sqrt{(1.07041)^2 + \left(1 - \frac{.66164}{\sqrt{3}}\right)^2} = 1.23606. \end{aligned}$$

The relative situations of the surrounding 13 points with respect to the selected point are of five kinds :

- (a) One point I lies on the trigonal axis which passes through the selected point H (comp. fig. 2).
- (b) Nearest to I and distant $2s$ from H are three similarly situated points J_1, J_2, J_3 , connected by successive rotations through 120° about the trigonal axis.
- (c) Next in order of distance from I and distant $2r$ from H are three points K_1, K_2, K_3 , similarly connected by the trigonal axis.
- (d) Next in order, distant $2s$ from H, three points L_1, L_2, L_3 , similarly connected.
- (e) Further from I and distant $2r$ from H, three points M_1, M_2, M_3 , similarly connected.

Since the distance of each point from the nearest corner of its cubic cell is n , and it lies on one of the trigonal axes, the value of a projection of n in each of the axes x, y, z is

$$\frac{n}{\sqrt{3}} = \frac{.33082}{1.73205} = .191 \text{ very approximately.}$$

The coordinates of each point, as referred to the angle of the cubic element in which it lies as origin, have this value ; and the coordinates of the 14 points, taking the centre of symmetry O, midway between the points H and I, as origin, and x, y, z parallel to cube edges as axes, are easily obtained and are as follows :—

		<i>x.</i>	<i>y.</i>	<i>z.</i>
For H, the point selected as centre of the polyhedral cell. $x = \frac{1}{2} - \cdot 191$	=	+ ·309	+ ·309	+ ·309
	I	- ·309	- ·309	- ·309
Nearest triad to I	{ J ₁	- ·691	- ·309	+ ·691
	{ J ₂	- ·309	+ ·691	- ·691
	{ J ₃	+ ·691	- ·691	- ·309
Next nearest triad to I	{ K ₁	+ ·691	+ ·309	- ·691
	{ K ₂	+ ·309	- ·691	+ ·691
	{ K ₃	- ·691	+ ·691	+ ·309
For next triad	{ L ₁	+ ·691	+ 1·309	- ·309
	{ L ₂	+ 1·309	- ·309	+ ·691
	{ L ₃	- ·309	+ ·691	+ 1·309
Further from I	{ M ₁	+ ·691	+ ·309	+ 1·309
	{ M ₂	+ ·309	+ 1·309	+ ·691
	{ M ₃	+ 1·309	+ ·691	+ ·309

B.

For finding the coordinates of the points of intersection of the planes drawn as prescribed to form a single polyhedral cell.

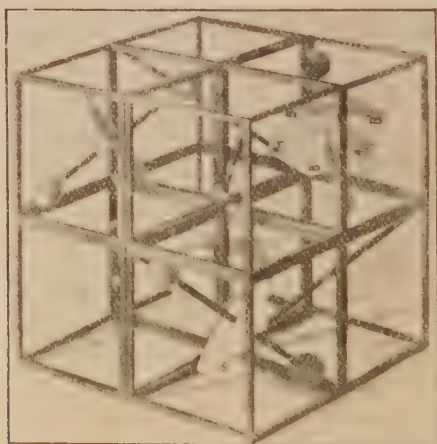
These points are, as already stated, 19 in number and are at the centre of spheres circumscribing irregular tetrahedra outlined by joining appropriate sets of four of the points just located. Three of these spheres, however, pass through more than four of the points: they circumscribe octahedra, each of which is outlined by joining six of these points, appropriately chosen, each octahedron possessing a single trigonal axis.

Now, as already pointed out, the existence of a centre of symmetry at the centre of each cubic element and of a single trigonal axis of rotation passing through this centre involves a sixfold regular hexagonal repetition of any point not a singular-point, which is present in the plane that passes through the centre of symmetry at right angles to the axis.

Let the 6 points of meeting of the plane bisecting the line HI at right angles with other pairs of the bisecting planes, which 6 points thus form the angular points of a regular hexagon, be lettered A', A'', A''', B', B'', B''' ; the three A's and also the three B's are related by the trigonal axis, while the B's are derivable from the A's by an operation about the centre of symmetry referred to situated at the centre of the cubic cell. The hexagonal interface thus

defined separates and is a common face of two enantiomorphous cells having the mirror image relation consequent on the presence of the centre of symmetry. Such interfaces are found in one only of the two systems of edge-contact cubic cells which together constitute the entire system of these cells filling space: namely, in the set containing the points of the fundamental point-system: they each indicate the only six points of intersection found in the cell containing it. Plane hexagons of appropriate size, cut out of cardboard, can be fixed, one in each of the cells in which these points are present, so as to show the

Fig. 4.



situations of a number of the points of intersection (fig. 4). Details enabling this to be done will be given immediately.

Other points of intersection of the planes, all of which are singular points above referred to, are found in the complementary set of cubic elements which do not contain any points of the fundamental point-system. These other points of intersection are situated three on each of the portion of a trigonal axis contained within each of the cubic elements of this complementary set. The central point of the three is at the centre of symmetry of the containing cubic cell; the other two points of a trio are equidistant from this centre of symmetry in positions determined later.

(a) As to the relative situations of the hexagonally-arranged group of 6 points of intersection present in the cubic cell with centre O :

The centre of the sphere circumscribing the tetrahedron outlined by lines joining points...

	H, I, J ₁ , K ₂ is lettered	A
.. .. .	H, I, J ₂ , K ₃	A'
.. .. .	H, I, J ₃ , K ₁	A''
.. .. .	I, H, K ₁ , J ₂	B'
.. .. .	I, H, K ₂ , J ₃	B''
.. .. .	I, H, K ₃ , J ₁	B'''

The relative situations and orientations of some of the other hexagonal plane groups of points of intersection found, one group in each of the cubic cells of the half-system of these cells containing points of the fundamental point-system, will now be considered.

The cubic cell containing the origin O, which point is the centre of the complex consisting of the pair of enantiomorphous cells having the hexagonal interface A', A'', A''', B', B'', B''' in common, is surrounded by 12 cubic cells in edge-contact with this central cell and occupied in the same manner. Each of these cubic cells bears the same relation as the central cell does to the unlimited system. These 12 cells are all equidistant from the origin O; they form six pairs, each consisting of two cells so related that one is developable from the other by operating the centre of symmetry at O. Otherwise considered they may be regarded as forming four sets, the individuals of each set of three being related by the trigonal axis passing through O. As to two of these sets, each of the three cells forming the set is so constituted and related that a corner of each and a corner of the central cell all four coincide on the trigonal axis passing through O. And as to the remaining two sets, the centres of all six cells lie hexagonally arranged in the plane which cuts the trigonal axis at right angles in the point O. The respective orientations of the 12 cubic cells referred to and the situation of their contents are conveniently arrived at by operating appropriate digonal screw coincidence movements which locate the 12 centres of the cells and their respective trigonal axes with reference to the position and orientation of the central cubic cell and its contents. This work can, however, be curtailed somewhat by resorting to the use of the centre of symmetry O. A general statement of the process employed for locating a hexagonal group in each of the 12 cubic cells, accompanied

by precise dimensions, is given in tabular form later (p. 944). In each case the appropriate digonal screw movement about an axis, having one of the three directions of the edges of the cubic cells, is resolved into a rotation of 180° about an axis in the same direction, which passes through the origin O, followed by two translations of $+1$ or -1 , as the case may be, in two of the three axial directions, such being chosen as to direction and value as are found to furnish appropriate components.

(b) As to those points of intersection of the planes which are *singular-points* lying on trigonal axes within the complementary sets of cubic elements which do not contain points of the fundamental point-system :

The centre of the sphere circumscribing the tetrahedron outlined by joining the 4 points	H, M ₁ , M ₂ , M ₃	is lettered	C ₀
" " "	K ₁ , J ₂ , L ₁ , H	" "	C ₁
" " "	K ₂ , L ₂ , J ₃ , H	" "	C ₂
" " "	K ₃ , J ₁ , L ₃ , H	" "	C ₃

The centre of the skeleton cube containing the point C₀ is equidistant from 6 points of the fundamental point-system and is the centre of the sphere circumscribing the octahedron located by these points; it is lettered D₀

That containing the point	C ₁	is lettered	D ₁
" " "	C ₂	" "	D ₂
" " "	C ₃	" "	D ₃

The coordinates of the points of intersection of the various planes drawn as indicated are ascertained in the following manner :—

As to A'.

Three of the planes passing through this point respectively bisect at right angles three lines joining nearest points of the point-system, viz. HK₂, LJ₁, and J₁K₂. And since these three lines are parallel to the planes yz , xz , and xy respectively, the three planes are respectively parallel to axis x , axis y , and axis z .

Draw three planes through the origin O parallel to these three planes. As a consequence of this parallelism :

In the case of the first plane the ratio $\frac{y}{x}$, in that of the second $\frac{x}{z}$, in the case of the third $\frac{x}{y}$ is constant for every point in the parallel plane.

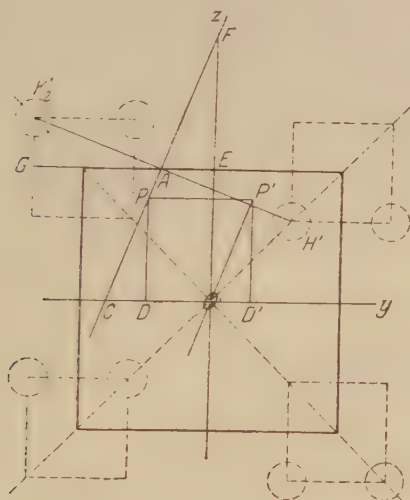
The other points of intersection possess a similar property, and as a consequence the work of ascertaining the coordinates

of all the points of intersection is comparatively simple. The following is the process in detail in the case of A' .

In fig. 5, $H'K_2'$ is the projection of the line HK_2 on plane yz to which plane this line is parallel, and CAF is the trace of the plane perpendicular to the line through its middle point. Through the origin O draw OP' parallel to CAF and PP' parallel to axis y through any point P in the trace CAF , the coordinates of this point being x, y, z .

Also PD and $P'D'$ parallel to axis z .

Fig. 5.



Then

$$\begin{aligned} \frac{D'O}{D'P'} &= \tan OP'D' = \tan CPD = \tan AFE \\ &= \tan K_2'AG = \frac{.191}{\frac{1}{2}} = .382. \end{aligned}$$

But $\frac{D'O}{D'P'}$ also $= \frac{CD}{DP}, \frac{OC-OD}{z} = \frac{OC+y}{z} = .382.$

Again,

$$\frac{AE}{EF} = \tan AFE = .382$$

$$\text{and } AE = EG - AG = (.5 + .191) - .5 = .191;$$

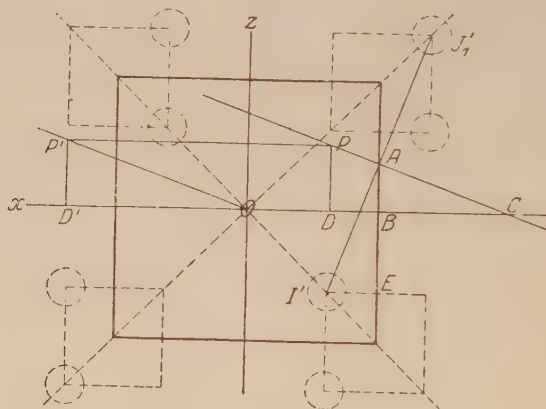
$$\therefore EF = \frac{AE}{\tan AFE} = \frac{.191}{.382} = .5 = EO = \frac{OF}{2}$$

$$\text{and } OC = 2AE = .382;$$

$$\therefore \frac{OC+y}{z} = \frac{.382+y}{z} = .382 \text{ and } y = -.382(1-z). \quad (1)$$

Again, fig. 6 gives the projection $I'J_1'$ of the line IJ_1 on plane xz and the trace CAP of the plane perpendicular to this line through its middle point.

Fig. 6.



Through the origin O draw OP' parallel to this trace and PP' parallel to axis x through any point P in this trace, the coordinates of this point being $-x$ and z ; also $P'D'$ parallel to axis z .

Then

$$\frac{D'O}{D'I'} = \tan OP'D' = \tan CPD = \tan AI'E = \frac{\frac{1}{2}}{\cdot 191} = \frac{1}{\cdot 382};$$

and

$$\frac{D'O}{D'P'} = \frac{DC}{DP} = (\text{since } x = -OD) \frac{OC + x}{z}.$$

Now

$$\frac{AB}{BC} = \tan ACB = \tan I'AE = \frac{\cdot 191}{\cdot 5} = \cdot 382$$

and

$$AB = AE - BE = \cdot 5 - (\cdot 5 - \cdot 191) = \cdot 191,$$

$$\therefore BC = \cdot 5.$$

And since

$$OB = \cdot 5, \quad OC = 1, \quad \text{and} \quad PP' = DD' = 1,$$

$$\therefore \frac{OC + x}{z} = \frac{1 + x}{z} = \frac{D'O}{D'P'} = \tan AI'E = \frac{1}{\cdot 382}$$

$$\text{and} \quad z = \cdot 382(1 + x). \quad \dots \dots \dots (2)$$

TABLE giving method of derivation of the relative situations and orientations, and also the respective coordinates of the constituent points, of 12 next surrounding hexagonal groups of points of intersection from the situation and orientation of the group found in the central cell containing the origin O, which group as above ascertained consists of the 6 points:—

- (1) A', the coordinates of which are $x = -.0955$, $y = -.25$, $z = +.3455$.
 (2) A'', " " " $-.25$, $+.3455$, $-.0955$.
 (3) A''', " " " $+.3455$, $-.0955$, $-.25$.
 (4) B', " " " $+.0955$, $+.25$, $-.3455$.
 (5) B'', " " " $+.25$, $-.3455$, $+.0955$.
 (6) B''', " " " $-.3455$, $+.0955$, $+.25$.

Designation of point the coordinates of which are required.	Derived from point designated.	Result of application of component rotation of 180° about axis of the appropriate screw spiral movement.							The required coordinates developed by the screw movement.		
		Axial direction.	Derived coordinates after rotation only.			Component translations added.					
			<i>x.</i>	<i>y.</i>	<i>z.</i>	<i>x.</i>	<i>y.</i>	<i>z.</i>	<i>x.</i>	<i>y.</i>	<i>z.</i>
A ₁ '	A'	<i>x</i>	-.0955	+.25	-.3455	+1	0	+1	+.9045	+.25	+.6545
A ₁ ''	A''	"	-.25	-.3455	+.0955	+1	0	+1	+.75	-.3455	+1.0955
A ₁ '''	A'''	"	+.3455	+.0955	+.25	+1	0	+1	+1.3455	+.0955	+1.25
B ₁ '	B'	"	+.0955	-.25	+.3455	+1	0	+1	+1.0955	-.25	+1.3455
B ₁ ''	B''	"	+.25	+.3455	-.0955	+1	0	+1	+1.25	+.3455	+.9045
B ₁ '''	B'''	"	-.3455	-.0955	-.25	+1	0	+1	+.6545	-.0955	+.75
A ₂ '	A'	<i>y</i>	+.0955	-.25	-.3455	+1	+1	0	+1.0955	+.75	-.3455
A ₂ ''	A''	"	+.25	+.3455	+.0955	+1	+1	0	+1.25	+1.3455	+.0955
A ₂ '''	A'''	"	.3455	-.0955	+.25	+1	+1	0	+.6545	+.9045	+.25
B ₂ '	B'	"	-.0955	+.25	+.3455	+1	+1	0	+.9045	+1.25	+.3455
B ₂ ''	B''	"	-.25	-.3455	-.0955	+1	+1	0	+.75	+.6545	-.0955
B ₂ '''	B'''	"	+.3455	+.0955	-.25	+1	+1	0	+1.3455	+1.0955	-.25
A ₃ '	A'	<i>z</i>	+.0955	+.25	+.3455	0	+1	+1	+.0955	+1.25	+1.3455
A ₃ ''	A''	"	+.25	-.3455	-.0955	0	+1	+1	+.25	+.6545	+.9045
A ₃ '''	A'''	"	-.3455	+.0955	-.25	0	+1	+1	-.3455	+1.0955	+.75
B ₃ '	B'	"	-.0955	-.25	-.3455	0	+1	+1	-.0955	+.75	+.6545
B ₃ ''	B''	"	-.25	+.3455	+.0955	0	+1	+1	-.25	+1.3455	+1.0955
B ₃ '''	B'''	"	+.3455	-.0955	+.25	0	+1	+1	+.3455	+.9045	+1.25
A ₄ '	A'	<i>x</i>	-.0955	+.25	-.3455	-1	0	-1	-1.0955	+.25	-1.3455
A ₄ ''	A''	"	-.25	-.3455	+.0955	-1	0	-1	-1.25	-.3455	-.9045
A ₄ '''	A'''	"	+.3455	+.0955	+.25	-1	0	-1	-.6545	+.0955	-.75
B ₄ '	B'	"	+.0955	-.25	+.3455	-1	0	-1	-.9045	-.25	-.6545
B ₄ ''	B''	"	+.25	+.3455	-.0955	-1	0	-1	-.75	+.3455	-1.0955
B ₄ '''	B'''	"	-.3455	-.0955	-.25	-1	0	-1	-1.3455	-.0955	1.25

coordinates of which are required.	Derived from point designated.	Result of application of component rotation of 180° about axis of the appropriate screw spiral movement.									The required coordinates developed by the screw movement.		
		Axial direction.	Derived coordinates after rotation only.			Component translations added.							
			x.	y.	z.	x.	y.	z.	x.	y.	z.		
A	A'	x	+0955	-25	-3455	-1	-1	0	-9045	-125	-3455		
A	A''	"	+25	+3455	+0955	-1	-1	0	-75	-6545	+0955		
A	A'''	"	-3455	-0955	+25	-1	-1	0	-13455	-10955	+25		
B	B'	x	-0955	+25	+3455	-1	-1	0	-10955	-75	+3455		
B	B''	"	-25	+3455	-0955	-1	-1	0	-125	-13455	-0955		
B	B'''	"	+3455	+0955	-25	-1	-1	0	-6545	-9045	-25		
A	A'	x	+0955	+25	+3455	0	-1	-1	+0955	-75	-6545		
A	A''	"	+25	-3455	-0955	0	-1	-1	+25	-13455	-10955		
A	A'''	"	-3455	+0955	-25	0	-1	-1	-3455	-9045	-125		
B	B'	x	-0955	-25	-3455	0	-1	-1	-0955	-125	-13455		
B	B''	"	-25	+3455	+0955	0	-1	-1	-25	-6545	-9045		
B	B'''	"	+3455	-0955	+25	0	-1	-1	+3455	-10955	-75		
A	A'	x	-0955	+25	-3455	+1	0	-1	+9045	+25	-13455		
A	A''	"	-25	-3455	+0955	+1	0	-1	+75	-3545	-9045		
A	A'''	"	+3455	+0955	+25	+1	0	-1	+13455	+0955	-75		
B	B'	x	+0955	-25	+3455	+1	0	-1	+10955	-25	-6545		
B	B''	"	+25	+3455	-0955	+1	0	-1	+125	+3455	-10955		
B	B'''	"	-3455	-0955	-25	+1	0	-1	+6545	-0955	-125		
A	A'	y	+0955	-25	-3455	-1	+1	0	-9045	+75	-3455		
A	A''	"	+25	+3455	+0955	-1	+1	0	-75	+13455	+0955		
A	A'''	"	-3455	-0955	+25	-1	+1	0	-13455	+9045	+25		
B	B'	y	-0955	+25	+3455	-1	+1	0	-10955	+125	+3455		
B	B''	"	-25	-3455	-0955	-1	+1	0	-125	+6545	-0955		
B	B'''	"	+3455	+0955	-25	-1	+1	0	-6545	+10955	-25		
A	A'	z	+0955	+25	+3455	0	-1	+1	+0955	-75	+13455		
A	A''	"	+25	-3455	-0955	0	-1	+1	+25	-13455	+9045		
A	A'''	"	-3455	+0955	-25	0	-1	+1	-3455	-9045	+75		
B	B'	z	-0955	-25	-3455	0	-1	+1	-0955	-125	+6545		
B	B''	"	-25	+3455	+0955	0	-1	+1	-25	-6545	+10955		
B	B'''	"	+3455	-0955	+25	0	-1	+1	+3455	-10955	+125		
A	A'	x	-0955	+25	-3455	-1	0	+1	-10955	+25	+6545		
A	A''	"	-25	-3455	+0955	-1	0	+1	-125	-3455	+10955		
A	A'''	"	+3455	+0955	+25	-1	0	+1	-6545	+0955	+125		
B	B'	x	+0955	-25	+3455	-1	0	+1	-9045	-25	+13455		
B	B''	"	+25	+3455	-0955	-1	0	+1	-75	+3455	+9045		
B	B'''	"	-3455	-0955	-25	-1	0	+1	-13455	-0955	+75		
A	A'	y	+0955	-25	-3455	+1	-1	0	+10955	-125	-3455		
A	A''	"	+25	+3455	+0955	+1	-1	0	+125	-6545	+0955		
A	A'''	"	-3455	-0955	+25	+1	-1	0	+6545	-10955	+25		
B	B'	y	-0955	+25	+3455	+1	-1	0	+9045	-75	+3455		
B	B''	"	-25	-3455	-0955	+1	-1	0	+75	-13455	-0955		
B	B'''	"	+3455	+0955	-25	+1	-1	0	+13455	-9045	-25		
A	A'	z	+0955	+25	+3455	0	+1	-1	+0955	+125	-6545		
A	A''	"	+25	-3455	-0955	0	+1	-1	+25	+6545	-10955		
A	A'''	"	-3455	+0955	-25	0	+1	-1	-3455	+10955	-125		
B	B'	z	-0955	-25	-3455	0	+1	-1	-0955	+75	-13455		
B	B''	"	-25	+3455	+0955	0	+1	-1	-25	+13455	-9045		
B	B'''	"	+3455	-0955	+25	0	+1	-1	+3455	+9045	-75		

Thus

$$x\{1-(\cdot382)^3\} = (\cdot382)^3 - (\cdot382)^2.$$

Now

$$1-(\cdot382)^3 = \cdot944257$$

$$\text{and } (\cdot382)^3 - (\cdot382)^2 = -\cdot09018.$$

Therefore the coordinates of A' are very approximately

$$x = -\frac{\cdot09018}{\cdot944257} = -\cdot0955,$$

$$y = \frac{x}{\cdot382} = \frac{\cdot0955}{\cdot382} = -\cdot25,$$

$$z = \cdot382(1+x) = \cdot382 \times \cdot9045 = \cdot3455.$$

The coordinates of the remaining five points of intersection of the same group, A'', A''', B', B'', B'', are deduced from those of A' ($x = -\cdot0955$, $y = -\cdot25$, $z = \cdot3455$) as follows :

A rotation with clock-hands of 120° about the trigonal axis of 120° which transfers axis y to the position of axis x carries A' to the position of A'', and a second such rotation locates the position of A'''. Therefore writing z for x , x for y , and y for z , we deduce from the coordinates of A' just stated,

those of A'' : $x = -\cdot25$, $y = +\cdot3455$, $z = -\cdot0955$;
and those of A''' : $x = +\cdot3455$, $y = -\cdot0955$, $z = -\cdot25$.

Further, by operating the centre of symmetry at O we derive from the coordinates of A' those of B' :

$$x = +\cdot0955, \quad y = +\cdot25, \quad z = -\cdot3455 ;$$

from those of A'' the coordinates of B'' :

$$x = +\cdot25, \quad y = -\cdot3455, \quad z = +\cdot0955 ;$$

and from those of A''' the coordinates of B''' :

$$x = -\cdot3455, \quad y = +\cdot0955, \quad z = +\cdot25.$$

The coordinates of the six points of each of the 12 hexagonal groups, found respectively in the 12 cubic cells having edge-contact with the central cell, are obtained as in the Table from those just recorded by means of the appropriate screw-movements above referred to (p. 939), the results being in some cases facilitated by operating with the centre of symmetry O.

Besides the above there are, as already intimated, present in the complex consisting of 8 cubic elements two other types of points of intersection of the planes, both of which lie on trigonal axes and are consequently singular points. Those four which are marked C_0, C_1, C_2, C_3 are, as in the previous cases, tetrahedron centres, the four solid angles of the tetrahedra being points of the fundamental point-system. The remaining points of intersection, four of which are marked D_0, D_1, D_2, D_3 in the model, lie at the centres of spheres circumscribing octahedra outlined by joining nearest points in certain octahedral complexes consisting of six points of the point-system. These points of intersection are found at the centres of the half of the cubic elements not containing any points of the fundamental point-system. The required coordinates are derived as follows:—

As to C_0 .

The coordinates of this point, which is the centre of the sphere circumscribing the tetrahedron H, M_1, M_2, M_3 are ascertained as follows:—

The tetrahedron is very symmetrical, three of its edges forming an equilateral triangle M_1, M_2, M_3 , and the

Fig. 8 a.

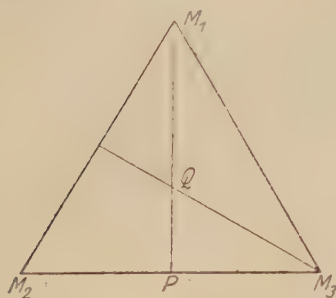
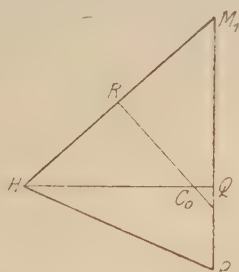


Fig. 8 b.



angular point H being equidistant from M_1, M_2, M_3 . Fig. 8 a represents the equilateral base, fig. 8 b a section through M_1QP containing the trigonal axis HC_0Q about which M_1, M_2, M_3 are symmetrically disposed.

$$M_1M_2 = M_2M_3 = M_3M_1 = 2s \quad (\text{see p. 936})$$

$$\text{and } HM_1 = HM_2 = HM_3 = 2r \quad (\text{see p. 936}).$$

The coordinates of C_0 are

$$x = y = z = \frac{OC_0}{\sqrt{3}}.$$

Now $OC_0 = OH + HC_0$ and $OH = r$,

while (fig. 8 *b*)

$$HC_0 = \frac{HR}{\cos C_0HR} = \frac{r}{\cos QHM_1};$$

but (see fig. 8 *a*)

$$\begin{aligned} \sin QHM_1 &= \frac{M_1Q}{HM_1} = \frac{\frac{s}{\cos 30^\circ}}{2r} = \frac{2s}{2r\sqrt{3}} \\ &= \frac{1.23606}{1.07041 \times 1.73205} = .667, \end{aligned}$$

and consequently

$$\angle QHM_1 \text{ or } C_0HM_1 = 41^\circ 50'.$$

Therefore

$$\begin{aligned} OC_0 &= r + \frac{r}{\cos C_0HM_1} = r \left(1 + \frac{1}{\cos 41^\circ 50'} \right) \\ &= r \left(1 + \frac{1}{.7450881} \right) = (.535205) \left(\frac{1.7450881}{.7450881} \right) = 1.2535. \end{aligned}$$

And the coordinates of C_0 are

$$+.72371; \quad +.72371; \quad +.72371.$$

As to C_1, C_2, C_3 .

The coordinates of C_0 are as above derived :

$$x = y = z = .72371 = .5 + .22371.$$

On examination of the models represented by figs. 2, 3, and 10, it is found that

The coordinates of C_1 are	$x =$	$.5 - .22371 = .27629$
	$y =$	$.5 + .22371 = .72371$
	$z =$	$-(.5 - .22371) = -.27629.$
.. .. C_2 are	$x =$	$.5 + .22371 = .72371$
	$y =$	$-(.5 - .22371) = -.27629$
	$z =$	$.5 - .22371 = .27629.$
.. .. C_3 are	$x =$	$-(.5 - .22371) = -.27629$
	$y =$	$.5 - .22371 = .27629$
	$z =$	$.5 + .22371 = .72371.$

Finally as to the coordinates of the centre points of the cubic cells not containing any points of the fundamental point-system.

The coordinates of D_0 : $x = y = z = 1$;

„ „ D_1 : $x = 0, y = 1, z = 0$;

„ „ D_2 : $x = 1, y = 0, z = 0$;

„ „ D_3 : $x = 0, y = 0, z = 1$.

C.

To find the lengths of the various edges of the polyhedral cells formed.

These edges, which in a single cell are 30 in number, are in their relations to the system as a whole of four kinds only:

- a.* Those which form sides of the hexagonal faces. These faces, it will be remembered, are found in those of the skeleton cubes which contain points of the fundamental point-system. Nine such sides or edges are found on each polyhedral cell; six of them form sides of its hexagonal face and the remaining three are sides of hexagonal faces of the adjoining cells.
- b.* Those which connect a point of the kind C situated on a trigonal axis with the nearest corner of a hexagonal face. Nine of these edges are found in each cell. Three of them meet on its axis as at point C_0 ; three others connect three angular points of its hexagonal face with other points of the kind C; the remaining three connect points of the hexagonal faces in adjoining cells with points of the kind C.
- c.* Those which coincide with some trigonal axis connecting a point of kind C with a corresponding point of kind D. Of these edges there are three in each cell.
- d.* Those which connect each angular point of a hexagonal interface with the nearest centre of kind D. Of these edges there are nine in each cell; three of them have respectively an extremity at three alternate angles of the hexagonal face of the selected cell; and the remaining six are connected with angles of hexagonal faces of neighbouring cells.

As to the length of those of kind *a* :—

Since the side of a hexagonal face equals the line joining its centre with one of its angular points, its length is

$$\sqrt{x^2 + y^2 + z^2} \text{ (as stated for the point of intersection } A') \\ = \sqrt{(-.0955)^2 + (-.25)^2 + (.3455)^2} = \sqrt{.191} = .43702.$$

As to that of kind *b* :—

For finding the edge which connects an angle of a hexagonal face with a nearest point of the kind *C*, *e. g.*, A_1' with C_0 :

$$\begin{array}{lll} \text{The coordinates of } A_1' \text{ are } & \overset{x.}{+.9045}, & \overset{y.}{+}.25, & \overset{z.}{+}.6545, \\ \text{and those of } C_0 \text{ are } & +.72371, & +.72371, & +.72371. \end{array}$$

Thus edge $A_1'C_0$

$$\begin{aligned} &= \sqrt{(.9045 - .72371)^2 + (.72371 - .25)^2 + (.72371 - .6545)^2} \\ &= \sqrt{(.18079)^2 + (.47371)^2 + (.06921)^2} \\ &= \sqrt{.032685 + .224401 + .00479} = \sqrt{.261476} = .51135. \end{aligned}$$

Another such edge $B''C_3$ calculated in the same manner gives an identical result.

As to that of kind *c* :—

For finding the edge which coincides with a trigonal axis ; for example, that which connects C_0 with D_0 the centre of the skeleton cube containing C_0 and D_0 :

$$\begin{array}{lll} \text{The coordinates of } C_0 \text{ are } & \overset{x.}{+.72371}, & \overset{y.}{+.72371}, & \overset{z.}{+.72371}, \\ \text{and those of } D_0 \text{ are } & +1, & +1, & +1. \end{array}$$

Thus edge C_0D_0 , which lies outside the cell figured,

$$\begin{aligned} &= \sqrt{(1 - .72371)^2 + (1 - .72371)^2 + (1 - .72371)^2} \\ &= \sqrt{3(.27629)^2} = .47855. \end{aligned}$$

The edges of kind *c* of the cell represented in fig. 10 are C_1D_1 , C_2D_2 , C_3D_3 : they furnish results identical with that just obtained for C_0D_0 .

As to that of kind *d* :—

For finding the edge which connects an angle of a

hexagonal face with the nearest cube centre of the kind D ; for example, the line A'D₃ :

The coordinates of A' are $-\overset{x}{.0955}, -\overset{y}{.25}, +\overset{z}{.3455},$
and those of D₃ are $0, 0, 1.$

Thus edge A'D₃

$$= \sqrt{(\cdot0955)^2 + (\cdot25)^2 + (1 - \cdot3455)^2}$$

$$= \sqrt{\cdot00912 + \cdot06250 + \cdot42837} = \sqrt{\cdot5} = \cdot707107.$$

The edges of kind *d* of the cell represented are A'D₃, A''D₁, A'''D₂.

D.

To find the shapes of the polygonal faces of a cell other than the hexagonal face.

This is accomplished by dividing these faces into triangles. The sides of the triangles which are not edges are diagonals of the polygons : their lengths are ascertained in the same manner as those of the cell-edges.

There are seven sets of these lines, examples of each set being

A'C₃, B'''D₃, A'B₁''', A₁C₂, C₂D₃, B''D₃, B''B₁''' respectively (fig. 9).

Fig. 9 a.

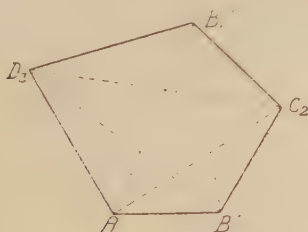
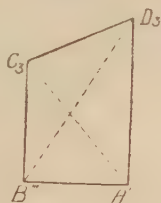


Fig. 9 b.



Three of these in conjunction with the lengths of the edges suffice for ascertaining the shapes of the irregular faces ; but it has to be borne in mind that a face of an ascertained shape and position bears a different relation to the two enantiomorphous forms of cell between which it is found.

As already intimated, there are but three kinds of interfaces : a hexagonal, a quadrilateral, and a five-sided.

All seven sets of face diagonals are here ascertained for the purpose of checking the accuracy of the calculations.

For finding $A'C_3$:

The coordinates of A' are $-.0955, -.2500, .3455$;
those of C_3 are $-.27629, +.27629, .72371$.

Thus $A'C_3$

$$\begin{aligned} &= \sqrt{(\cdot27629 - \cdot0955)^2 + (\cdot2500 + \cdot27629)^2 + (\cdot72371 - \cdot3455)^2} \\ &= \sqrt{(\cdot18079)^2 + (\cdot52629)^2 + (\cdot37821)^2} \\ &= \sqrt{\cdot032685 + \cdot27698 + \cdot143042} = \sqrt{\cdot452707} = \cdot67283. \end{aligned}$$

For finding $B'''D_3$:

The coordinates of B''' are $-.3455, .0955, .25$;
those of D_3 are $0, 0, 1$.

Thus $B'''D_3$

$$\begin{aligned} &= \sqrt{(\cdot3455)^2 + (-\cdot0955)^2 + (1 - \cdot25)^2} \\ &= \sqrt{\cdot11937 + \cdot00912 + \cdot56250} = \sqrt{\cdot69099} = \cdot83126. \end{aligned}$$

For finding $A'B_1'''$:

The coordinates of A' are $-.0955, -.2500, +.3455$;
those of B_1''' are $+.6545, -.0955, +.7500$.

Thus $A'B_1'''$

$$\begin{aligned} &= \sqrt{(\cdot0955 + \cdot6545)^2 + (\cdot2500 - \cdot0955)^2 + (\cdot7500 - \cdot3455)^2} \\ &= \sqrt{(\cdot7500)^2 + (\cdot1545)^2 + (\cdot4045)^2} \\ &= \sqrt{\cdot5625 + \cdot02387 + \cdot16362} = \sqrt{\cdot7500} = \cdot86602. \end{aligned}$$

For finding $A'C_2$:

The coordinates of A' are $-.0955, -.2500, +.3455$,
those of C_2 are $+.72371, -.27629, +.27629$.

Thus $A'C_2$

$$\begin{aligned} &= \sqrt{(\cdot0955 + \cdot72371)^2 + (\cdot27629 - \cdot2500)^2 + (\cdot3455 - \cdot27629)^2} \\ &= \sqrt{(\cdot81921)^2 + (\cdot02629)^2 + (\cdot06921)^2} \\ &= \sqrt{\cdot67111 + \cdot00069 + \cdot00479} = \sqrt{\cdot67659} = \cdot82255. \end{aligned}$$

For finding C_2D_3 :

The coordinates of C_2 are $+.72371, -.27629, +.27629$,
those of D_3 are $0, 0, 1$.

Thus C_2D_3

$$= \sqrt{(\cdot 72371)^2 + (\cdot 27629)^2 + (\cdot 72371)^2}$$

$$= \sqrt{2(\cdot 52375) + \cdot 076336} = \sqrt{1\cdot 123836} = 1\cdot 0601.$$

For finding $B''D_3$:

The coordinates of B'' are $+\cdot 2500, -\cdot 3455, \cdot 0955$,
those of D_3 are $0, 0, 1$.

Thus $B''D_3$

$$= \sqrt{(\cdot 2500)^2 + (\cdot 3455)^2 + (\cdot 9045)^2}$$

$$= \sqrt{\cdot 06250 + \cdot 11937 + \cdot 81812} = \sqrt{1} = 1.$$

Finally, for finding $B''B_1'''$:

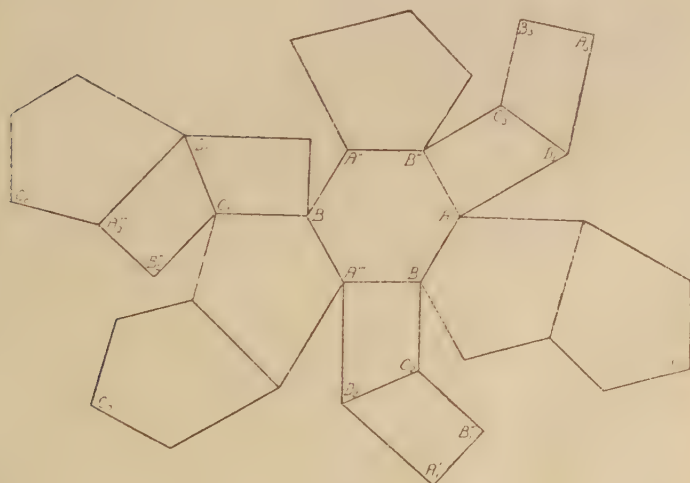
The coordinates of B'' are $+\cdot 2500, -\cdot 3455, \cdot 0955$,
those of B_1''' are $+\cdot 6545, -\cdot 0955, \cdot 7500$.

Thus $B''B_1'''$

$$= \sqrt{(\cdot 4045)^2 + (\cdot 2500)^2 + (\cdot 6545)^2}$$

$$= \sqrt{\cdot 16362 + \cdot 06250 + \cdot 42837} = \sqrt{\cdot 65449} = \cdot 8090.$$

Fig. 10.



E.

Finally, as to the construction of a "mat."

Fig. 9 (p. 951) shows the three kinds of cell faces derived from the foregoing ; and fig. 10 is a plan of the relative

situations of the 13 faces of a single cell as presented when they are hinged at their edges and folded down so as to lie in one plane.

A model of a cell is obtained from this plane diagram by transferring the arrangement shown to a sheet of cardboard and marking on this all the boundary lines of the faces as in fig. 10; then cutting half through the cardboard along all these lines and folding up the various polygons in such a way as to bring together lines representing the same edge. Selvages are left so as to attach corresponding boundaries securely. Cells of the two enantiomorphous forms are shown in fig. 3. The same "mat" serves for both enantiomorphous forms if the marking on the face of the diagram shows through at the back: the process employed at the face for the one form is similarly employed at the back for the other. This involves the mirror-image resemblance of the two forms.

The fitting of a number of the cells together so as to have no interstices is a simple matter if they are first paired so that the two cells of a pair have contact at their hexagonal faces, one being the image-mirror of the other, and the two being so adjusted as to be related by a centre of symmetry as shown in fig. 3, not by a plane of symmetry.

The author has called attention to the applicability of the space-partitioning here described to the case of a crystal of potassium chloride, the symmetry of which is regarded as hemihedral-cubic (Proc. Roy. Soc. A, vol. xci., 1914, p. 1) The geometrical representation given by him can be regarded as an extension of the method of graphic formulae employed by the organic chemist, undertaken for the purpose of representing crystal structure. The following points of resemblance between the artificial structure above described and the properties of the potassium chloride crystal are discernible:—

1. The similarity as to form and number of the two component enantiomorphous sets of cells renders them available for representing equality both of number and valency of the atoms of potassium and chlorine.
2. The cells form pairs, the enantiomorphous individuals of a pair being intimately and specially associated. A close attachment of two atoms, one of each kind, to form a molecule is thus pictured. The atomic arrangement according to a cubic lattice which has been previously suggested as the interpretation of the

experimental facts, fails in this respect since any choice of pairs of nearest points of this lattice to represent molecules is necessarily arbitrary and inconsistent with cubic symmetry.

3. The distances of the points found in the same skeleton cube from its centre being equal, the molecular centres are represented by the centres of half the skeleton cubes so selected as to be in edge-contact. This is the arrangement assigned by Bragg to the molecular centres.

The artificial system presents, however, if the allotment to the same kind of atom is uniform throughout, a lower class of symmetry than that assigned to the crystal, viz. tetartohedry not hemihedry. This discrepancy may be attributed to intimate twinning, which is capable of closely mimicking the higher class of symmetry.

Ewing's well-known experiment with a flock of freely suspended magnets is suggestive in connexion with the system described:—If magnets were freely suspended one in each pair of cells with its centre at the centre of the hexagonal interface separating them, their interaction might well produce stable equilibrium symmetrically related to the system of non-intersecting axes.

The foregoing is a particular case of an infinite series of partitionings each of which is based on some regular point-system the points of which form pairs, the two individual points of a pair lying within the same cubic cell of a half-system of cubic cells throughout which the cubes are in contact at edges only and being found on the same trigonal axis equidistant from the cell centre. The condition as to equality of joining lines differently related to the system which characterizes the particular case is absent in the other partitionings.

It is interesting to observe that the limiting cases between which the infinite series referred to lies are:—

(α) That in which the two points of each pair lie precisely at opposite corners of a cubic cell on its non-intersecting trigonal axis; the point-system developed is a cubic space-lattice and the partitioning results in a regular system of cubic cells. If planes perpendicular to the trigonal axes and bisecting each line joining the points of a pair are added to the other bisecting planes, as in the instance given above, each cubic cell will be so bisected as to produce a hexagonal interface which is at right angles to its single non-intersecting

trigonal axis, and the two halves of a cell will be enantiomorphs and bear a mirror-image relation to each other.

(β) That in which the two points of each pair coalesce at the centre of a cubic cell of the half-system just referred to, thus constituting a face-centred cubic space lattice. The hexagonal faces here fall to zero and disappear and the cells are rhombic dodecahedra.

All of the infinite series except the two limiting cases present hemihedral cubic symmetry.

XCIX. *On the X-Ray Spectra of Hafnium and Thulium.*
By D. COSTER*.

[Plate XIII.]

IN a series of letters to 'Nature' † Hevesy and the present writer announced the discovery of the element of atomic number 72, and published some general data as regards the occurrence and chemical properties of this element, for which the name hafnium was proposed. It is the purpose of this note to give some more details about the physical methods used during our investigation. At the same time I am glad to use this occasion to complete the tables of wave-lengths of X-ray lines for the elements hafnium and thulium.

According to the Bohr theory of atomic structure ‡, the element of atomic number 72 must be homologous to titanium, zirconium, and thorium. As the elements in the neighbourhood of 72 (lanthanum, tantalum, tungsten) are very closely related to their homologues in the neighbourhood of zirconium (*i. e.*, yttrium, niobium, and molybdenum respectively), it seemed to be rational to expect that as regards its chemical properties the element 72 should be very closely related to zirconium, and that it eventually might be found in combination with this element. We therefore investigated the X-ray spectrum of zirconium minerals and of zirconium preparations, and we were able to prove that the substance ordinarily known as zirconium is not a pure element, but a mixture of two elements: for the greater part one of atomic number 40 and (usually in an amount of 1 to 5 per cent.) one of atomic number 72.

* Communicated by Prof. N. Bohr.

† D. Coster and G. Hevesy, 'Nature,' vol. cxi. pp. 79, 182, 252, 462 (1923).

‡ See N. Bohr, 'Theory of Spectra and Atomic Constitution,' Cambridge, 1922.

During our investigations we used a vacuum spectrograph for relative measurements, constructed according to a design kindly furnished by Professor Siegbahn to this Institute. Using a Norwegian mineral, we were able to detect six lines of the L-series of the element 72. In Table I. are given our provisional results, which were published in 'Nature.' In the second column stand the values found by interpolation between the wave-lengths for the elements Cp (71) and Ta (73).

TABLE I.

Provisional Results for the L-Series of Hafnium *.

	Measured.	Interp.
α_2	1576	1576.9
α_1	1565.5	1565.9
β_1	1371.4	1371.0
β_3	1350.2	1349.5
β_2	1323.7	1323.1
γ_1	1677	1176.4

Not only was the agreement very close as regards the numerical values for the wave-lengths, but also the relative intensities of the different lines agreed with expectations. The presence of the element 72 in zirconium minerals and preparations was therefore established beyond all doubt. For the element 72 we proposed the name "hafnium," whereas it seemed to be reasonable to keep the name "zirconium" for the element of atomic number 40, which, in general, forms by far the greatest part of the zirconium as known before.

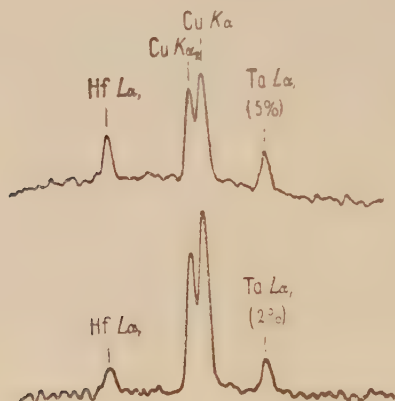
In order to get some idea about the concentration of hafnium in the different zirconium minerals and preparations, the following method was used. A known quantity of the element of atomic number 73 (tantalum) was added to the preparation, and an X-ray spectrum was taken of the mixture. By comparing the intensity of the hafnium lines with that of the corresponding tantalum lines, estimates of considerable accuracy were obtained as to the concentration of hafnium in the preparations. The reliability of this method follows from the same reasons that allow us to understand the great similarity of the X-ray spectra of different elements. Indeed, the X-ray lines are emitted during transition processes between stationary states by which electrons in the inner part of the atom take part,

* Cf. 'Nature,' vol. cxi. p. 79 (1923).

and the conditions at the outside of the atom have no appreciable influence on these processes. We may therefore expect that the intensity of X-ray lines is simply proportional to the number of atoms present in the anticathode spot*.

The method is illustrated by figs. 1, 2, and 3. They are photometer curves obtained by measurements of the plates with a Moll photometer. Fig. 1 relates to the investigation

Fig. 1.



of zirconium minerals. The upper curve on this figure is taken from a Ural zirconium mineral, the lower from a Brazil mineral. The first mineral seems to contain about 5 per cent. Hf, the other a little less than 2 per cent. Fig. 2 shows how the chemical properties of hafnium were studied. A solution of a mixture of zirconium and hafnium in strong acids was precipitated with sodium phosphate in eleven subsequent fractions, each containing the same amount of insoluble phosphate. To every fraction 10 per cent. of tantalum was added. The curve at the top is taken from the spectrum of the first fraction, the next curve from the fourth fraction, and the bottom curve from the eighth fraction. We may conclude from these curves that hafnium phosphate is even less soluble than zirconium phosphate. Figure 3 gives a control to the method. Two artificial preparations were made by adding SnCl_2 and Sb_2O_3 to calcium phosphate. Both preparations contained 10 per cent.

* For a closer discussion of the matter, see D. Coster, *Chemical News*, vol. cxxvii. p. 65 (1923).

Fig. 2.

Cu $K\alpha$

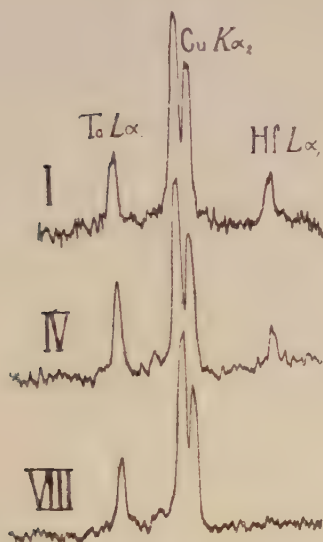
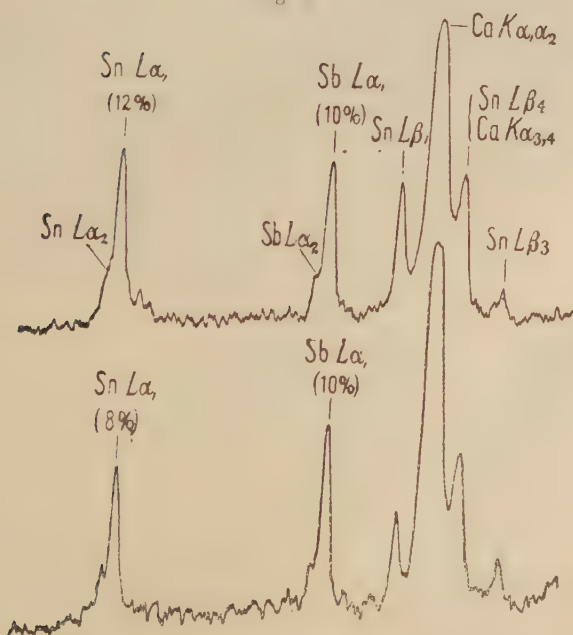


Fig. 3.



antimony, whereas 12 per cent. tin was added to the first fraction and 8 per cent. tin to the second fraction. The curves actually show that the amount of antimony in the first case is smaller and in the second case larger than the amount of tin present in the preparation.

With the aid of methods described by Hevesy *, hafnium preparations were obtained which contained only small amounts of zirconium (less than 5 per cent.). One of these preparations was used to take strongly-exposed X-ray spectra with calcite as analysing crystal throughout the whole region of the L-series. Besides, some lines of the M-series were exposed, using gypsum as analysing crystal. The wavelengths measured from these plates are given in Table II.

TABLE II.
L-Series of Hafnium.
Emission Spectrum.

Line.	Glancing angle, Calcite.	λ .	$\frac{\nu}{R}$.	$\sqrt{\frac{\nu}{R}}$.
l	17 3 39	1777.4	512.70	22.643
α_2	15 5 21	1577.04	577.84	21.038
α_1	14 58 54	1566.07	581.89	24.125
η	14 31 40	1519.7	599.66	24.488
β_4^1	13 15 28	1389.3	655.91	25.611
$\beta_1-\beta_0$...	13 4 53	1371.1	664.60	25.780
β_3	12 52 22	1349.7	675.20	25.985
β_2	12 37 10	1323.5	688.51	26.238
β_7	12 25 33	1303.5	699.08	26.440
γ_5	11 32 31	1212.1	751.80	27.419
γ_1	11 11 54	1176.5	774.55	27.831
γ_2	10 51 32	1141.3	798.46	28.257
γ_3	10 48 16	1135.6	802.48	28.328
γ_4	10 27 47	1100.1	827.68	28.769

¹ Confounds with $K\beta_1$ of Cu.

The lines L_{α_1} and L_{α_2} were determined by Mr. Hjalmar in the laboratory of Professor Siegbahn, using a spectrograph for absolute measurements with the aid of a hafnium preparation provided by us. His results were kindly put at our disposal. They agree very well with the results obtained by Mr. Žáček in the same laboratory †. The error in the wavelengths of these lines is less than 0.1 X-unit. The other

* G. Hevesy, *Chemische Berichte*, lvi., p. 1503 (1923); *Chemical News*, cxxvii. p. 33 (1923).

† *Zs. für Phys.* vol. xv. p. 31 (1923).

TABLE III.

L-Series of Hafnium.

Absorption Spectrum.

Limit.	Glancing angle, Calcite.	λ .	$\frac{\nu}{R}$.	$\sqrt{\frac{\nu}{R}}$.
L_I^1	0 25 " 7	1097	830.70	28.822
L_{II}	10 57 28	1151.5	791.37	28.131
L_{III}	12 19 25	1293.0	704.77	26.547

¹ Confounds with L_{γ_1} of W.

TABLE IV.

M-Series of Hafnium.

Line.	Glancing angle, Gypsum.	λ .	$\frac{\nu}{R}$.	$\sqrt{\frac{\nu}{R}}$.
α	29 45 " 6	7521	121.15	11.008
β	28 44 19	7286	125.06	11.183

lines in the L-series were measured relatively to the α -lines or to the copper or tungsten lines appearing on the same plates. Here the error will be in most cases less than 0.4 X-units. The wave-lengths of the lines of the M-series which were determined with a gypsum crystal are less accurate. Here the error may be of the order of magnitude of 2 X-units. Plate XIII. gives the reproduction of most of the lines in the L-series. The lines γ_4 and γ_5 lie outside the region exposed. The copper lines are due to the copper of the anticathode, the tungsten lines are due to the tungsten sputtered by the hot wire.

Besides the lines and absorption limits given in Table II., also the K-absorption limit of hafnium is known. This was measured by de Broglie and Caprera * shortly after our discovery of the presence of the element 72 in zirconium minerals was announced. In their investigation de Broglie and Caprera used as absorbing substance a zirconium mineral which obviously contained a rather high percentage of hafnium. They found the value 190.5 X-units.

It might be of some interest to discuss the question of how to identify the two X-ray lines found by Dauvillier† in a preparation of rare-earth metals and ascribed to a rare-earth element cerium, the presence of which in this preparation

* *Comptes Rendus*, vol. clxxvi. p. 433 (1923).† *Comptes Rendus*, vol. clxxiv. p. 1347 (1922).

was suspected by Urbain. The wave-lengths given by Dauvillier for these lines are 1561·8 and 1319·4 X-units respectively. The differences between these wave-lengths and those given in Table II. for the hafnium lines L_{γ_1} and L_{β_2} are 4·3 and 4·1 X-units respectively, which correspond to distances on Dauvillier's plates of about 0·7 mm., 1 mm. corresponding to 6 X-units. The wave-lengths of the lines of the elements Yb and Cp found by Dauvillier on the same plates on which the cerium lines were detected, however, agree closely with those found by the writer. If in the special case of the Ct lines we accept differences of 4·3 X-units between the precision measurements from Siegbahn's laboratory and Dauvillier's measurements, we get the following other possibilities for the identification of the same lines :—

1561·8 : 2nd order	Zr- K_{α_1} , Sr- K_{β_1} ,
3rd	„ Pd- K_{β_1} .
4th	„ Ba- K_{α_2} , I- K_{β_1} ;
1319·4 : 1st	„ Pt- L_{γ_2} , Ta- L_{β_1} .
3rd	„ I- K_{α_2} ,
4th	„ Nd- K_{α_1} .

None of these possibilities were discussed in Dauvillier's original paper *.

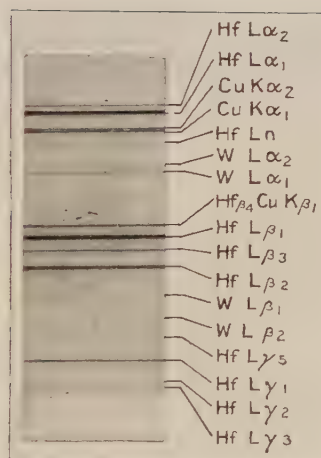
Identifying, however, Dauvillier's lines with lines of the element 72, we meet with the following difficulties. If the line 1319·4 should be L_{β_2} of hafnium, it is difficult to see why the line β_1 of the same element, which is stronger, was not visible on Dauvillier's plate †. Besides, the line 1561·8 which should be identifiable with Hf L_{α_1} was, according to Dauvillier, so faint that it was on the limit of visibility. In this case, however, it is scarcely probable that the much less intense line L_{β_2} of the same element should be visible at all.

In a former paper ‡, I gave the results of the measurements

* *Comptes Rendus*, vol. clxxiv. p. 1347 (1922). In a later discussion of our results as regards the identification of the element 72, however, Dauvillier (*Comptes Rendus*, vol. clxxvi. p. 676 (1923)) discusses the possibilities Ta, Zr, Pd, Ba, Nd, but not Pt, Sr, or I.

† A photograph taken of a mixture of the elements Hf and Cp showed that the line Hf L_{β_1} does not coincide with any Cp-line as was thought by Dauvillier. The lines Hf L_{β_1} and Cp L_{β_2} lie at a distance of more than 4 X-units from one another, which is nearly the same distance as the distance of the two copper lines K_{α_1} and K_{α_2} on Plate XIII., whereas the satellite which Dauvillier found at a distance of 1 X-unit from Cp L_{β_2} and which he calls Cp L_{β_2}' could not be detected by us even on a very strongly exposed plate.

‡ Phil. Mag. xlv. p. 546 (1922).



Hf L-SPECTRUM.

of the lines in the L-series of all the elements from La to Cp, with the exception of those with atomic numbers 61 and 69. The element 61 is unknown, while 69 is usually identified with the rare-earth element thulium, which possesses an atomic weight between that of Er (68) and that of Yb (70). In the spectrum of the same Yb-Cp preparation of Urbain, in which Dauvillier found the two lines ascribed to the element 72, he also detected three very weak lines which he identified with the lines β_2 , γ_1 and γ_2 of the element of atomic number 69. The amount of the element 69 in Dauvillier's preparation, however, was very small, and no direct evidence was obtained as to whether this element is the same as the element thulium, known by its optical spectrum and chemical properties. Therefore I have undertaken an investigation of a concentrated thulium preparation kindly put at our disposal by Dr. Auer von Welsbach. The X-ray spectrum showed that this preparation actually consisted almost entirely of the element of atomic number 69. Also the presence of a little ytterbium and of a trace of erbium could be detected. The results of the measurements are given in Table V.

TABLE V.
L-Series of Thulium.

Line.	Glancing angle, Calcite.	λ .	$\frac{\nu}{R}$.	$\sqrt{\frac{\nu}{R}}$.
λ	18 47 19	1951.1	467.05	21.611
a_2	16 36 36	1733.9	525.57	22.926
a_1	16 31 24	1722.8	528.93	22.998
η	16 12 21	1692.3	538.49	23.212
β_4 ¹	14 44 17	1541.2	591.26	24.316
β_1	14 35 53	1526.8	596.84	24.431
β_6	14 26 53	1511.5	602.90	24.554
β_3	14 21 28	1502.3	606.60	24.629
β_2	13 56 51	1460.2	624.10	24.982
γ_5	12 53 54	1352.3	673.88	25.959
γ_1	12 30 50	1312.7	694.23	26.348
γ_2	12 6 48	1271.2	716.83	26.291
γ_3 ²	12 3 20	1265.3	720.22	26.837
γ_4 ³	11 40 47	1226.4	743.03	27.259

¹ Coincides with $K\alpha_2$ of Cu.

² Coincides with $L\gamma_1$ of Yb.

³ Coincides with $L\gamma_3$ of Yb.

Institute for Theoretical Physics,
Copenhagen,
August 1923.

*C. The Stark Effect for Strong Magnetic Fields.**To the Editors of the Philosophical Magazine.*

GENTLEMEN,—

ON the pages of your esteemed Magazine there has recently appeared an argument on the above subject between Messrs. A. M. Mosharrafa (xliii. p. 493; xlv. p. 371, 1922) and H. O. Newbould (xlv. pp. 1681, 1923), resulting in a discrepancy of opinions between them. Both those authors seem not to have been familiar with the writer's earlier work on the same subject. In fact, the term of the Stark effect depending on the square of the electric force was computed and published by myself several years ago (*Annalen d. Physik*, li. p. 184, 1916). My formula is identical with that given last year by Mosharrafa, and therefore in disagreement with Newbould's result. After the appearance of his paper I checked my computations and confirmed them.

Permit me to add that Mr. Takamine's interesting observations on the Stark effect in strong fields were discussed before Mosharrafa by Sommerfeld (*Annalen d. Physik*, 1920), who pointed out that they can be accounted for by my formula.

PAUL S. EPSTEIN.

Norman Bridge Laboratory of Physics,
Pasadena (Calif.), June 6th, 1923.

CI. *The Electronic Theory of Valency.*—Part II. *Intramolecular Ionization in Organic Compounds.* By Professor T. MARTIN LOWRY, C.B.E., M.A., D.Sc., F.R.S.*

1. *Intramolecular Ionization in Inorganic Compounds.*

IN the preceding paper of this series † I directed attention to the fact that the electronic theory of valency permits of a very wide extension of Thomson's theory of intramolecular ionization, and that polar bonds may be detected in a large range of inorganic compounds where it has been generally assumed hitherto that the linkages are all of a

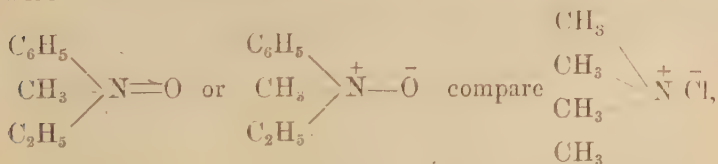
* Communicated by the Faraday Society.

† Trans. Faraday Soc. xviii. p. 285 (1923); Phil. Mag. [6] xlv. p. 1105 (1923).

non-polar or covalent type. In particular, a study of the electronic formulæ of Langmuir reveals the fact that, whilst there is usually a perfect balance between the nuclear charge of each atom and the enveloping shell of electrons, in other cases the negative charge of the shell is either too large or too small to balance exactly the positive charge of the nucleus. Thus, in the case of CO_2 and N_2O (adopting Lewis's symbols for the double bonds), the analysis of the charges works out as follows :—

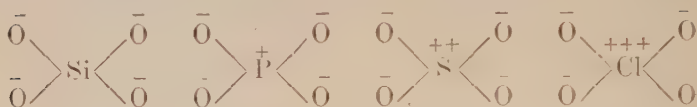
	$:\ddot{\text{O}}:$	$:\text{C}:$	$:\ddot{\text{O}}:$	$:\ddot{\text{O}}:$	$:\text{N}:$	$:\ddot{\text{N}}:$
K-electrons... ..	2	2	2	2	2	2
L-electrons,						
shared ($\div 2$) ...	2	4	2	2	4	2
unshared.....	4	0	4	4	0	4
Total electrons ...	8	6	8	8	6	8
Nuclear charge ...	8	6	8	8	7	7
Resultant charge .	0	0	0	0	+1	-1

The residual charges thus detected in Langmuir's formula for nitrous oxide were represented by writing the compound as $\text{O}=\overset{+}{\text{N}}-\overset{-}{\text{N}}$ or $\text{O}=\overset{-}{\text{N}}\equiv\overset{+}{\text{N}}$, where the barb represents an electrovalency passing from the positively to the negatively charged atom*. Intramolecular ionization was also detected in Langmuir's formulæ for the amine oxides, which were written as follows :—



* This formula for nitrous oxide shows the active bond as joining two nitrogen atoms. The behaviour of the gas is, however, much more like that of an oxide of N_2 , reacting in the form $\overset{-}{\text{O}}-\overset{+}{\text{N}}\equiv\text{N}$, although the familiar ring-formula $\begin{array}{c} \text{N} \\ | \\ \text{N} \end{array} \rangle \text{O}$ is also a possible alternative as a picture of the molecule in its resting phase. The argument from isosterism may be met by pointing out that benzene and thiophen, which do not even contain the same number of atoms or of planetary electrons, resemble one another even more closely than do CO_2 and N_2O .

and for the ions of the oxy-acids H_4SiO_4 , H_3PO_4 , H_2SO_4 , and HClO_4 , which were written as



2. Application to Organic Compounds.

An extensive application of the theory of intramolecular ionization to organic compounds is rendered possible by taking advantage of a more recent conception of Sir J. J. Thomson. He suggests that the reactivity of double bonds in organic chemistry may be attributed to the fact that it is easier to open the hinge between two cubical octets sharing a common face* than to break the hinge which holds together two octets sharing only a common edge. This view can scarcely be accepted as an adequate explanation of the reactivity of double bonds, since fluorine is in fact far more reactive than oxygen; but if the assumption be made that the rupture of the double bond takes place unsymmetrically, so as to leave 8 L-electrons on one atom and only 6 on the other †, a very suggestive system of formulæ is arrived at, in which ethylene is represented as containing a "mixed double bond," whilst acetylene can be represented in a similar way as containing a "mixed triple bond." These formulæ may be analysed, just as in the case of Langmuir's formulæ for CO_2 and N_2O , as follows:—

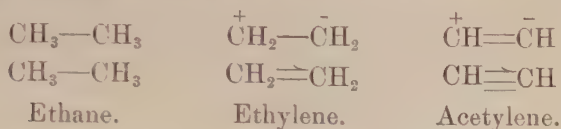
	Ethane.		Ethylene.		Acetylene.	
	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H} : \ddot{\text{C}} : \ddot{\text{C}} : \text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$		$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H} : \ddot{\text{C}} : \ddot{\text{C}} : \text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$		$\begin{array}{c} \text{H} : \text{C} :: \ddot{\text{C}} : \text{H} \end{array}$	
K-electrons	2	2	2	2	2	2
L-electrons						
shared ($\div 2$) ...	4	4	3	3	3	3
unshared	0	0	0	2	0	2
Total electrons ...	6	6	5	7	5	7
Nuclear charge ...	6	6	6	6	6	6
Resultant charge..	0	0	+1	-1	+1	-1

In view of the electric charges which are disclosed by this

* Compare Lewis, J. A. C. S. xxxviii, p. 778 (1916).

† Compare Lewis's view of the dissociation of the diatomic molecule of a halogen into an octet and a sextet, *loc. cit.* p. 775.

analysis, these formulæ may be written in a conventional form as follows :—



A large number of organic compounds have been formulated on these lines in a paper on "The Polarity of Double Bonds," which has recently appeared in the *Journal of the Chemical Society* *. These formulæ may be regarded, from one point of view, as merely introducing a uniform nomenclature to express a number of phenomena in organic chemistry which cannot be represented satisfactorily by Kekulé's non-polar or covalent bond. Hitherto it has been the rule to introduce a new nomenclature and a new symbolism to express each anomaly as it has been encountered, *e.g.* centric bonds in aromatic compounds, carbonium bonds, mobile hydrogen atoms, residual affinities, partial valencies, principal and subsidiary valencies, etc. Most of these anomalies can now be recognized as being due to the development of electrovalencies and a single symbolism may be used to express them all. The time is indeed ripe for chemists to state definitely how many types of valency they require the physicist to provide, and, in particular, whether in organic chemistry the non-polar tetrahedrally-arranged bonds of diamond, giving a distance of 1.5 Angström units between the centres of adjacent carbon atoms, and the electrovalent link † with its radiating fields of electrostatic force, are sufficient to express the facts of chemical combination, or whether these must be supplemented by half-a-dozen more types of linkage to cover special cases and anomalies.

The introduction of a uniform nomenclature and symbolism has, however, had the further effect of disclosing relationships between a number of phenomena which have hitherto appeared to be entirely independent of one another. Thus, reactivity in organic chemistry can now be ascribed to the same cause as reactivity in inorganic chemistry, namely to a process of ionization, although the ions in organic chemistry are usually "bound" instead of "free." Again, the theory of "crossed polarities," which follows directly from the symbolism now suggested, makes it possible to ascribe to a

* *Trans. Chem. Soc.* cxxiii. p. 822 (1923).

† This appears to give a distance between centres of 3.25 Å.U. in graphite.

common cause a series of chemical changes, in derivatives of maleic acid and of benzene respectively, which have hitherto been discussed separately, if discussed at all. In the same way, the theory of "multipolar ions" has disclosed a wholly unexpected relationship between the phenomena of dynamic isomerism and those of coordination. These correlations are of interest on general grounds; but their real value lies in the large amount of experimental work which they have already suggested.

3. *Reactivity and Activation of Organic Compounds.*

In describing to the Chemical Society* some of the consequences that follow from the theory that "a double bond in organic chemistry usually reacts as if it contained one covalency and one electrovalency," I laid considerable stress on the fact that the resting states of the molecule are not necessarily identical with their reactive phases. It is, therefore, not necessary to assume that a polar double bond always represents the most stable form of an unsaturated compound, nor that a "hinge" when once opened is incapable of closing up again.

The idea that many types of molecules undergo a preliminary process of activation before undergoing chemical change is an old one, and has been developed very largely by Arrhenius; but this idea has hitherto been mainly physical in character, since the problem has usually been studied from the standpoint of the amount of energy (*e. g.* the number of quanta of radiation) required to effect the activation, rather than of the chemical character of the processes involved. The views which are now put forward make it possible to assign, however, a definite chemical meaning to the process of activation, since it appears that in many cases this may consist simply in the conversion of covalent into electrovalent bonds. This is in accordance with the generally-recognized fact that ions will interact immediately without any preliminary process of activation. A very wide field of experimental research is thus opened out, and, if the views in question should prove to be well-founded, it will be possible to revive in a modern electronic form the theory of Armstrong that "chemical action is reversed electrolysis," since it would appear that "chemical action is ultimately an action between ions, either free or bound." The physico-chemical aspects of the theory of intramolecular ionization may therefore prove to be not less fertile than the purely chemical aspects.

* Trans. Chem. Soc. cxxiii. p. 822 (1923).

4. Polar Organic Compounds.

It is probable that organic compounds may be divided into two groups according as the normal structure of the molecule is polar and therefore reactive, or is non-polar and must undergo isomeric change into a polar form before it can react. Some examples of molecules which may be permanently polar are set out in the following paragraphs.

(a) *Organic-metallic Compounds*.—According to the electronic theory of valency, the lighter metals are only stable in the condition of ions: and the bonds which unite them to other elements are always of the nature of electrovalencies*. If this view be accepted, the metallic derivatives of organic radicles must all have a polar structure like that assigned to sodium chloride, $\bar{\text{Na}}\bar{\text{Cl}}$. From this point of view, zinc

methyl, $\overset{++}{\text{Zn}} \begin{array}{l} \nearrow \bar{\text{CH}}_3 \\ \searrow \bar{\text{CH}}_3 \end{array}$, and the Grignard reagent, $\overset{++}{\text{Mg}} \begin{array}{l} \nearrow \bar{\text{CH}}_3 \\ \searrow \bar{\text{I}} \end{array}$,

should exist only in a polar form, in which the methyl-groups are present as anions linked to the metallic kation by electrostatic forces. This does not mean that these compounds must necessarily yield conducting solutions, since it must be remembered that an ionizing solvent is generally required in order to enable the ions to separate to such a distance that they can move in opposite directions under the influence of electrostatic forces, instead of clinging together, *e. g.* as an electrically-neutral doublet. Failing the discovery of a suitable ionizing solvent, experiments on the ionization-potentials of the vapours of some of these metallic compounds would be of great interest.

(b) *Metallic Salts*.—Similar considerations apply in the case of metallic derivatives of a more commonplace character, such as sodium ethoxide, $\overset{+}{\text{Na}}\bar{\text{O}}.\text{C}_2\text{H}_5$, sodium phenate, $\overset{+}{\text{Na}}\bar{\text{O}}.\text{C}_6\text{H}_5$, or sodium acetate, $\overset{+}{\text{Na}}\bar{\text{O}}.\text{CO}.\text{CH}_3$. In the first of these compounds, the radicle attached to the oxygen atom of the anion is saturated, and there is no reason to suppose that this can easily assume a polar character: although, if a rupture were actually to take place between oxygen and carbon or between carbon and carbon, it is probable that the general rule would be followed that under these conditions a covalency gives rise to an electrovalency,

* The heavier metals, on the other hand, may be covalent in their coordination-compounds.

i. e. to a sextet and an octet rather than to two septets. On the other hand, in sodium phenate and sodium acetate, the radicle attached to the oxygen is unsaturated in the sense that it is commonly represented as containing one or more "double bonds." These double bonds can be pictured as capable of changing over into a polar form and, although it may be difficult to provide absolute proof, it is reasonable to suppose that the polarity of the $\overset{+}{\text{Na}}\overset{-}{\text{O}}$ group may be transmitted to the remainder of the conjugated system and that, for instance, sodium acetate may normally exist in the fully-

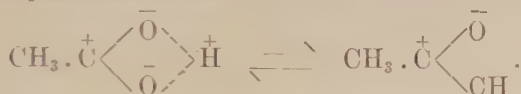
polar form, $\overset{+}{\text{Na}} \begin{array}{c} \diagup \text{O} \diagdown \\ | \\ \text{O} \end{array} \text{C}^+ \cdot \text{CH}_3$.

(c) *Quinquevalent Nitrogen as a Key-atom*.—From the considerations set out above it will be seen that the metals may play a very important part as "key-atoms" in maintaining the "induced alternated polarities" of a conjugated molecule*. A similar part may sometimes be assigned to oxygen in view of the limitation, which is generally assumed to be inherent in the octet theory, of the number of covalencies to four in the case of elements of small atomic number. I have already quoted in a note to the Chemical Society the case of methylethylaniline oxide, $\text{C}_6\text{H}_5 \cdot \text{N}^+ \text{MeEt} \cdot \text{O}^-$, where a reversion of the double bond between nitrogen and oxygen to a non-polar form would involve the production of a quinquevalent atom of nitrogen: in that case I have suggested that the double bond may be permanently polar in character, and that the nitrogen must always carry a positive charge, just as in the commoner ammonium salts, such as ammonium chloride, $\overset{+}{\text{NH}}_4\text{Cl}$. Similar considerations suggest that the nitro-group, which I have written as $\overset{-}{\text{O}} = \overset{++}{\text{N}} = \overset{-}{\text{O}}$, is incapable of assuming the non-polar condition indicated by the formula $\text{O} = \text{N} = \text{O}$, although it might very well assume the cyclic

form $\text{N} \begin{array}{c} \diagup \text{O} \diagdown \\ | \\ \text{O} \end{array}$. Under these conditions the nitro-group may sometimes act (like ammonium) as a key-radicle in maintaining the polarity of a conjugated system: the action of nitro-groups in stabilizing the structure of benzene is indeed already recognized.

* Compare Lapworth, 'Manchester Memoirs,' lxiv, no. 2, p. 1 (1920); Trans. Chem. Soc. cxxi, p. 417 (1922).

(d) *Other Key-atoms.*—There is good reason for thinking that ionizable chlorine and ionizable hydrogen may also act as key-atoms in fixing the polarity of a conjugated system. This action is, however, less certain since chlorine and hydrogen are both capable of forming covalent bonds, and can therefore readily pass into a non-ionized form. Thus, if Hantzsch's views of the relationship between the fatty acids and their salts and esters are correct, a fatty acid in aqueous solution may be formulated as an equilibrium-mixture of true acid and pseudo-acid, thus



The ionization, which is permanent in the salts, may therefore be only temporary in the acid from which they are derived. It is, moreover, possible that, when the acidic hydrogen atom passes over from the coordinated to the hydroxylic form, the carbonyl group may also become non-polar, although I do not know of any experimental data by which this point can be decided.

5. Non-polar Organic Compounds.

(i.) It must be recognized that in general all fully saturated compounds are non-polar unless ionizable. Thus, an electrovalency can only be developed, in a system made up entirely of single bonds, by breaking one of the covalencies, and so producing two independent ions, instead of the bound ions that are formed by the rupture of the double bond. The reactivity of a saturated compound probably depends on the readiness with which this conversion of a covalency into an electrovalency can occur. In the same way the reactivity of an "unsaturated" compound may be measured by the readiness with which a double covalency can be converted into a "mixed double bond." In many cases this conversion is very difficult to effect; thus oxygen gas (although it contains a double bond and is capable of forming addition-compounds, *e.g.* with hydrogen gas) is not usually classed as unsaturated, since it is very inert and requires to be activated, *e.g.* by heat or by a catalyst, before it will unite with other elements, although it will unite in the cold with nitric oxide. In general it may be said that a compound which requires "activating" before it will react is probably in a non-polar condition, whilst instant reactivity suggests that the compound is already ionized, whether the ions are free or bound.

(ii.) In the absence of a metallic ion or other powerful key-atom there is no guarantee that the polar condition of the molecule will be maintained in its resting state. In the case of ethylene, although the polar formula clearly represents in a most effective way the mechanism of the interaction of the unsaturated hydrocarbon with ionizable reagents, definite evidence is now available to show that the hydrocarbon itself is inert. Thus, Stewart and Edlund, by investigating the rate of reaction between ethylene and bromine*, have established the fact that "reaction takes place for the most part, if not entirely, on the walls of the containing vessel," and "no evidence of gaseous reaction could be found." These conditions are very similar to those which prevail in the case of oxygen and hydrogen which, even when moist, will only react at atmospheric temperatures when in presence of a catalyst.

(iii.) The problem of deciding whether in other cases the resting form of the molecule is active or inactive is obviously one that must be settled by experiment, not by guessing, since there are at present not sufficient data to make it possible to establish any general rule. The observations of Stewart and Edlund are, however, sufficient to justify the view that the homologues of ethylene probably pass into a polar form only during chemical change; this renders possible a simpler explanation of their behaviour towards reagents than would be possible if the polar molecules represented the resting-state of the hydrocarbon. For instance, the production of by-products may be due, not to the reversal of an existing polarity, but to the double bond becoming polar in opposite senses to an extent which varies with the degree of polarity of the reagent. Thus propylene gives †

with HI 99½ % of $\text{CH}_3\text{.CHI.CH}_3$ to ½ % of $\text{CH}_3\text{.CH}_2\text{.CH}_2\text{I}$;

with ICl ... 75 % of $\text{CH}_3\text{.CHCl.CH}_2\text{I}$ to 25 % of $\text{CH}_3\text{.CHI.CH}_2\text{Cl}$;

with BrCl ... 58 % of $\text{CH}_3\text{.CHCl.CH}_2\text{Br}$ to 42 % of $\text{CH}_3\text{.CHBr.CH}_2\text{Cl}$.

6. Conjugation and Crossed Polarities.

(a) The theory of mixed double bonds gives a new interpretation to the phenomena of conjugation discussed by Thiele in 1899. It now appears that a conjugated compound is one which, in its reactive form, contains an unbroken series

* J. Amer. Chem. Soc. xlv. p. 1014 (1923).

† Michael, *J. prakt. Chem.* [2] lx. p. 445 (1899); *Ber.* xxxix. p. 2140 (1906).

of positive and negative charges on alternate atoms. This view differs fundamentally from Thiele's original conception, in that, whereas he chooses maleic acid as a typical example of conjugation, the new theory shows in this compound a discordant series of polarities, which destroys the conjugation of the system. On this point a definite experimental test of the theory can be made, since, if Thiele's view were correct, the maleic type of structure should be particularly stable, whilst in the light of the present theory the crossed polarities would render it relatively unstable, at least under conditions which tend to promote polarization of the molecule. I have already * directed attention to three cases in which derivatives of maleic acid get rid of this condition of crossed polarities by undergoing isomeric change to a compound in which the series of alternate single and double bonds is shorter, but in which the polarities are no longer discordant; I also quoted one case † in which the crossed polarities are rendered concordant by the loss of a molecule of carbon dioxide. In another group of cases, which has been studied intensively by Thorpe and his colleagues ‡, the crossed polarities are eliminated by the addition of water or of ethyl alcohol. In the absence of any alternative explanation of these changes, and especially in view of the fact that Thiele's views lead to a directly opposite conclusion, the series of cases quoted above may be regarded as decisive evidence in favour of the theory of polar double bonds.

(b) It is also of interest to notice the conditions under which these changes occur. Loss of carbon dioxide and gain of water and alcohol actually occur during the course of reactions carried out with a view to preparing acids of a maleic type: it is therefore likely that these changes take place whilst the molecule is in the reactive or polar form. When, however, a compound of a maleic type has been isolated, the isomeric changes that have been referred to above are brought about by boiling with strong caustic soda, *i. e.* under the very conditions that have been postulated (p. 970) as likely to drive a molecule over into a polar form. Opposite conditions can be achieved by converting the acid into its anhydride, since this not merely removes the sodium ions of the salt but also eliminates even the acidic hydrogen of the acid. All possibility of forming free ions is thus removed and, in the absence of these ionizable key-atoms, it is

* Trans. Chem. Soc. cxxiii. p. 825 (1923).

† *Ibid.*

‡ Trans. Chem. Soc. cxxi. p. 650 (1922).

doubtful whether even the polarity of the carbonyl groups would be maintained. It is precisely under these conditions that a double bond, which has been expelled from its original position under the influence of caustic soda, creeps back again into the ring and yields a derivative of maleic anhydride.

(c) A number of other cases are known in which strong caustic soda is used to bring about chemical or physical changes, *e. g.* a reversal of sign in the rotatory power of the tartrates. It will be of interest to inquire whether in these cases also the chemical changes demand the formation of a polarized molecule as an intermediate or final product, and whether the physical properties developed by the soda are those that might be expected in a molecule of this kind.

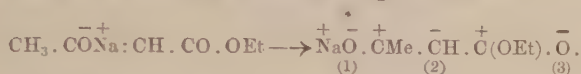
(d) In a totally different field crossed polarities afford a simple explanation of the mobility of aromatic groups which are "incorrectly" oriented, *e. g.* the *meta* nitro-group of β and γ trinitrotoluene. Apart from the theory of induced polarity, it is difficult to see any clear reason why nitro-groups occupying adjacent positions in the benzene ring should be so mutually antagonistic.

7. Multipolar Ions.

An important application of the theory of mixed double bonds is found in the discovery of the multipolar ion, *i. e.* of ions which, in addition to the electrification which is required to give the net charge of the ion, possess a series of additional positive and negative charges, so that, for instance, a univalent anion may contain *three* negatively charged atoms, alternating with *two* positively charged atoms, giving the net charge of minus *one*. This discovery has provided a novel interpretation of the phenomenon of tautomerism, and has disclosed a relationship between tautomerism and coordination which appears not to have been recognized previously, even by those who were working on these two phenomena separately, since no definite liaison had been established between these two independent lines of investigation.

(a) *Tautomeric Ions*.—It has usually been assumed that ethylacetoacetate can yield two ions, one derived from the ketonic form of the ester, and the other from the enolic form; and that the reversible isomeric change of the esters (which appears to demand the presence of a trace of an alkaline catalyst) involves both the migration of a mobile hydrogen ion and a structural rearrangement of the anion.

If, however, the views set out in paragraph 4 (*b*) above are adopted, it would appear that, in the sodium derivative at least, the metallic atom may act as the key-atom in setting up "induced alternating polarities" throughout the conjugated chain, as shown in the following scheme* :—



The ion of the ester is now seen to contain three negative poles. It is tautomeric, since if a hydrogen ion be attached to the negative pole 2 it will yield a ketone, whilst if attached to the negative pole 1 it will yield an enol having the formula conventionally assigned to this compound; if attached to the negative pole 3 it would yield an isomeric enol, in which the carboxyl-group instead of the ketonic-group has been enolized.

No evidence of the existence of a second enol has been discovered, and of this fact also the electronic theory provides a simple explanation, which I have discussed in a paper on "Coordinated Hydrogen" recently communicated to the Chemical Society†. This explanation is based on the assumption that in the sodium-derivative, a sodium ion is coordinated with two oxygen poles 1 and 3 in just the same way as in the metallic derivatives of acetylacetone‡; and that in the enol a hydrogen ion may be similarly coordinated. Since the distinction between principal and subsidiary valencies cannot be maintained, the coordinated forms of the two enols would be identical.

This coordinated enol may be expected, like the sodium derivative, to persist in a polarized form, since it owes its very existence as a stable isomer to the possibility of forming by coordination a conjugated six-atom ring; but even this apparently obvious conclusion ought to be confirmed by experiment. The ketonic form, on the other hand, like maleic anhydride, contains only two unconjugated carbonyl-groups, and may easily revert to a non-polar form. Indeed, it is possible that di-ketones of this type give rise in general to one polarized and one unpolarized form, and that these are represented by a fully-polar coordinated enolic and a non-polar ketonic form respectively.

* In the second formula the groups have been re-arranged so as to show the conjugated chain as the principal axis of the molecule.

† Trans. Chem. Soc. cxxiii. p. 2111 (1923).

‡ Morgan, Trans. Chem. Soc. cv. p. 193 (1914).

(b) *Coordination of Multipolar Ions.*—The importance of multipolar ions in the preparation of coordinated compounds has been pointed out in the Chemical Society paper already referred to *, and has been discussed more fully in a series of articles in 'Chemistry and Industry.' It will therefore suffice here to direct attention to the fact that we have already succeeded in preparing in this laboratory coordinated-derivatives of compounds which have been studied hitherto as examples of dynamic isomerism, and that the liaison between these two lines of investigation has provided another very fertile field of research.

8. *Summary.*

(a) The theory of intramolecular ionization can be extended to organic compounds if it be assumed that double bonds can assume a form in which one carbon atom carries *eight* L-electrons, but the other only *six*, one pair of electrons only being shared. Since the former atom is then negatively and the latter positively charged, this type of double bond may be represented as made up of one covalency and one electrovalency.

(b) This extension of the theory of intramolecular ionization brings the reactivity of organic compounds into line with the well-recognized activity of inorganic ions, and makes it possible to regard all chemical action as ultimately ionic in character.

(c) The resting forms of the molecules need not be identical with their ionized or reactive forms. Examples are given, however, of organic compounds which probably have a permanently ionized structure, comparable with that of metallic salts. In other cases evidence is quoted to show that this condition results from a definite process of activation.

(d) Attention is directed to several phenomena which receive a simple explanation in the "crossed polarities" of compounds which have hitherto been classed as "conjugated."

(e) The properties of "multipolar ions" are referred to as furnishing a basis for a novel theory of tautomeric ions, and an explanation of their readiness to yield coordination-compounds.

University Chemical Laboratory,
Cambridge.

* Trans. Chem. Soc. cxxiii. p. 830 (1923).

CII. *On the Theory of Light-Quanta.* By H. BATEMAN, Professor of Mathematics, Theoretical Physics, and Aeronautics, California Institute of Technology, Pasadena *.

IN a justly famous paper, in which he proposed his theory of the photoelectric effect, Einstein † showed that the idea of light-quanta is a plausible one when considered from the point of view of cavity radiation. For small densities of radiation of a definite frequency ν , Wien's radiation formula may be regarded as applicable, and it appears that the radiation of this frequency behaves as if it consisted of discrete quanta, of energy $h\nu$, spatially independent of each other.

Einstein's analysis has been recently extended by Wolfke ‡, who shows that Planck's radiation formula can be interpreted to mean that cavity radiation consists of a series of partial radiations thermodynamically independent of each other, the constituents of each order being distributed as regards frequency according to a law analogous to that of Wien. The density u of radiation whose frequency lies between ν and $\nu + d\nu$ is in fact, by Planck's law,

$$u = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{\frac{h\nu}{kT}} - 1} = \sum_{s=1}^{\infty} u_s,$$

where

$$u_s = \frac{8\pi h\nu^3}{c^3} e^{-\frac{sh\nu}{kT}}$$

is the density of a partial radiation of order s .

By a repetition of Einstein's argument, in which use is made of the formula

$$S = - \frac{kE_s}{sh\nu} \left(\log \frac{e^3 E_s}{8\pi h\nu^3 V} - 1 \right),$$

for the entropy S of a partial radiation of order s and energy $E_s = Vu_s$ contained in a volume V , Wolfke finds that the probability W_s that this energy may find itself at an arbitrary instant of time in the partial volume V' is

$$W_s = \left(\frac{V'}{V} \right)^{\frac{E_s}{sh\nu}},$$

* Communicated by the Author.

† *Ann. der Phys.* xvii. p. 132 (1905).

‡ *Phys. Zeitschr.* xxii. p. 375 (1921).

and concludes that the s th partial radiation is composed of $\frac{E_s}{sh\nu}$ spatially independent radiation quanta of energy $sh\nu$.

The analysis has recently been carried a step further by de Broglie*, who points out that Einstein's formula

$$\overline{\epsilon^2} = h\nu\overline{E} + \frac{c^3\overline{E}^2}{8\pi\nu^2Vd\nu},$$

for the mean value of the square of the deviation ϵ of the energy E (of radiation of frequencies ν to $d\nu$ contained in the volume V) from its mean value \overline{E} , can also be written in the form

$$\overline{\epsilon^2} = \sum_{s=1}^{\infty} sh\nu \overline{E}_s,$$

where \overline{E}_s is the mean value of E_s . The term of order s , viz. $sh\nu \overline{E}_s$, is just the value one would expect if the energy E_s were made up of $\frac{E_s}{sh\nu}$ light-quanta each of energy $sh\nu$.

The term $\frac{c^3\overline{E}^2}{8\pi\nu^2Vd\nu}$ in Einstein's formula, which represents the mean value of ϵ^2 when use is made of the idea of interfering waves of all possible amplitudes and phases distributed in frequency according to the Rayleigh-Jeans law, can also be supposed to arise from the coherence of "light-atoms" of energy $h\nu$ with the consequent formation of light-molecules, the energy of a "light-molecule" of order s being $sh\nu$. De Broglie concludes that if the quantum theory of light ever provides an interpretation of interference, it must introduce such "light-molecules."

In a later paper † de Broglie uses the methods of statistical mechanics to derive Wien's law of radiation from the hypothesis of discrete light-atoms. To obtain the correct numerical factor, he adopts Brillouin's suggestion that each light-atom is associated with an internal state of right- or left-handed circular polarization.

This indicates that a light-quantum may not be so essentially different from an electromagnetic field as some writers seem to expect. Indeed, if we imagine a light-quantum to be made up of superposed electromagnetic radiant fields of an elementary nature in which the light-vectors are transverse to the direction of motion of the quantum, the fact that

* *Comptes Rendus*, clxxv. p. 811 (1922).

† *J. de Physique et le Radium*, iii. p. 422 (1922).

we can apparently add the energies of coherent light-quanta may mean that from a statistical point of view the directions of the light-vectors in the constituent fields are distributed at random or it may mean that the fields do not overlap.

Adopting a well-known argument due to the late Lord Rayleigh, let us consider n equal light-vectors transverse to the direction of propagation and subject to the usual vector law of addition. The magnitude of the resultant vector ranges from zero, when the vectors are parallel to the radii from the centre of a regular polygon to its corners, to a maximum value when all the vectors have the same direction. The mean value of the square of the resultant in a random distribution is, however, n times the square of the magnitude of one of the constituents, so that the energies appear to be additive.

The electromagnetic analogy is strengthened, too, by the successful development by Stark *, Einstein †, and others ‡ of the idea that a concentrated form of momentum of magnitude $\frac{h\nu}{c}$ accompanies a light-quantum of energy $h\nu$, and has the same direction as the velocity of the quantum.

This relation between energy and linear momentum is a characteristic of all the forms of electromagnetic radiant fields that have been proposed as possible models of quanta.

From the point of view of the classical electromagnetic theory of Maxwell and Lorentz, a quantum consists of a radiant field of the ordinary type in which there is a concentration of energy in the initial stages of propagation, the distribution of energy becoming gradually more and more diffuse §.

In Sir Joseph Thomson's theory || the concentrated energy is imagined to be located in or around discrete Faraday tubes, and light is supposed to consist of waves or kinks travelling along these tubes.

Sir W. H. Bragg ¶ imagines that a form of electricity

* *Phys. Zeitschr.* x. p. 902 (1909), xi. pp. 24, 179 (1910).

† *Ibid.* x. pp. 185, 817 (1909), xviii. p. 121 (1917); *Ver. d. D. Phys. Ges.* xviii. p. 318 (1916).

‡ R. Emden, *Phys. Zeitschr.* xxii. p. 513 (1921). A. H. Bucherer, *ibid.* xx. p. 451 (1920); *Ann. d. Phys.* lxxviii. pp. 1, 546 (1922). A. H. Compton, *Phys. Review*, May 1923; W. Duane, *Proc. Nat. Acad.* vol. ix. p. 158 (1923).

§ An attempt to account for a concentration of energy on the basis of the classical theory has been made by R. A. Houston, 'Nature,' April 24, 1919, p. 145.

|| 'Electricity and Matter.' London, 1904.

¶ *Phil. Mag.* xv. p. 663 (1908), xvi. p. 918 (1908), xx. p. 385 (1910).

travels with the waves and is responsible for the concentration of energy and momentum.

The original idea of the "neutral pair" of electric charges was that it consists of an electron neutralized by a positively-charged particle, such as a proton, but on account of the fact that, according to the usual ideas, electrons and protons cannot travel with the velocity of light, it seems better to regard any electric charges that travel with waves of light as consisting of an entirely different form of electricity which can travel with the velocity of light and still be associated with finite amounts of energy and momentum. There is nothing unreasonable in this supposition, for the laws which determine the structures of the electron and proton may quite likely determine also a third form which can travel with the velocity of light and have either a positive or negative charge*.

The type of electricity we have in mind is not essentially different from the "ether" particles which are the carriers of electromagnetic fields of the ordinary type. The difference is simply one of degree, as we shall endeavour to show later on. Indeed, it is possible to adopt the view that the electric charges travelling with the waves are only convenient mathematical symbols for something which is quite compatible with the classical electromagnetic wave theory, the electric charges appearing only when a limiting process is carried out. There is some doubt as to whether this view is quite sound, but the point at issue will be brought out in the discussion.

Sir William Bragg has put forward an argument† in favour of the idea of the existence of actual electric charges in the waves which has never been satisfactorily answered. "The corpuscular form of the X- and γ -ray, and its energy relations to the β -ray which is its origin, and the β -ray which is its conclusion are the principal things which any theory must account for, and any model must illustrate. For this reason the spreading pulse of Stokes fails: and so does the kink in the tube of force of J. J. Thomson. The former diffuses its energy over a broadening surface, the latter over a lengthening line."

It is true that the rate at which the line lengthens may be very slow if the velocity of oscillation at the source of light is always very small, and the shape of a line of force is

* This is true, for instance, in the case of one law consistent with the theory of relativity and capable of furnishing discrete charges in uniform motion. *Phys. Review*, xx. p. 243 (1922); 'Nature,' April 28, 1923.

† British Association Report, 1911, p. 340.

determined by the classical theory *, but the author does not feel that this argument is quite sufficient to meet Bragg's objection. The objection fails, however, if we depart slightly from the classical theory and assume that a line of force (or, rather, a line round which radiant energy is concentrated) is generated by light-particles which are projected in a constant direction from the different positions of an oscillating charge. When such a theory of discrete Faraday tubes is adopted, it seems necessary to suppose that a form of electricity is radiated from an accelerated charge, for a continuous field in which the lines of force have the desired form is specified by equations of type †

$$H_x = \frac{\partial(\omega, \tau)}{\partial(y, z)}, \quad E_x = \frac{1}{c} \frac{\partial(\omega, \tau)}{\partial(x, t)}, \quad \dots \quad (1)$$

where

$$[x - \xi(\tau)]^2 + [y - \eta(\tau)]^2 + [z - \zeta(\tau)]^2 = c^2(t - \tau)^2$$

and

$$\omega = \frac{e}{4\pi} \frac{c^2 - \xi'^2 - \eta'^2 - \zeta'^2}{c^2(t - \tau) - (x - \xi)\xi' - (y - \eta)\eta' - (z - \zeta)\zeta'},$$

the primes denoting differentiations with respect to τ . In this field, electricity is radiated from the moving singularity $[\xi(\tau), \eta(\tau), \zeta(\tau)]$ with the velocity of light, and can be regarded as made up of electric dipoles.

When Poynting's vector is supposed to determine the flow of energy, it appears that there is no flow of energy to infinity in this continuous field even when the moving singularity has an accelerated motion. The field may thus furnish us with a crude model of the field of an electron describing a non-radiating orbit round a positive nucleus, but the model is probably not correct, because it is unlikely that the electric dipoles would move *freely* in the field of the positive nucleus. The field may still be of some service in predicting the behaviour of an atom under the influence of an external field, as will be seen later in a brief discussion of Prof. Whittaker's quantum mechanism in the atom.

If the theory of discrete Faraday tubes is developed somewhat in the manner suggested, it is not essentially different from that form of electromagnetic theory in which a concentration of radiant energy is associated with the presence of a form of electricity travelling with the waves. This form of electromagnetic theory may be regarded as due in the first

* Bull. Amer. Math. Soc. xxvii. p. 217 (1921).

† Proc. London Math. Soc. xviii. p. 95 (1919); Phil. Mag. xli. p. 107 (1921).

place to Sir W. H. Bragg, Oliver Heaviside*, and Levi Civita†.

A type of electromagnetic field which furnishes a simple working model of radiation with a concentration of energy may be specified by vectors \mathbf{E} and \mathbf{H} with components

$$\left. \begin{aligned} E_x = H_x = 0, \quad E_y = H_z = \frac{\partial \Omega}{\partial y} f\left(t - \frac{x}{c}\right), \\ E_z = -H_y = \frac{\partial \Omega}{\partial z} f\left(t - \frac{x}{c}\right), \end{aligned} \right\} \quad (2)$$

where Ω is a function of y and z whose derivatives are large near some point or points of the yz -plane and small elsewhere. Ω may even be zero in certain parts of the plane.

This radiation possesses many of the familiar properties of plane waves of light; thus \mathbf{E} and \mathbf{H} are perpendicular, equal in magnitude and transverse to the direction of propagation, but the direction of polarization generally varies over the wave-front.

Radiation of this type can, moreover, be obtained theoretically in a perfectly natural manner by the reflexion of "ordinary" plane waves of light at the surface of a mirror in the form of a paraboloid of revolution. This problem of reflexion will be treated here in an ideal fashion, for the paraboloid is supposed to extend to infinity and reflect perfectly; moreover, the amplitude of the incident waves is assumed constant over the wave-front, so that there is an infinite amount of energy in the incident waves. Reflexion at the paraboloid produces a concentration of an infinite amount of energy along the axis of the paraboloid and so a return radiation with a singular ray is to be expected.

To solve the problem, we represent the components of the electric force \mathbf{E} and magnetic force \mathbf{H} in the form

$$\left. \begin{aligned} H_x + iE_x &= f(\alpha, \beta) \frac{\partial(\alpha, \beta)}{\partial(y, z)} = \frac{i}{c} f(\alpha, \beta) \frac{\partial(\alpha, \beta)}{\partial(x, t)}, \\ H_y + iE_y &= f(\alpha, \beta) \frac{\partial(\alpha, \beta)}{\partial(z, x)} = \frac{i}{c} f(\alpha, \beta) \frac{\partial(\alpha, \beta)}{\partial(y, t)}, \\ H_z + iE_z &= f(\alpha, \beta) \frac{\partial(\alpha, \beta)}{\partial(x, y)} = \frac{i}{c} f(\alpha, \beta) \frac{\partial(\alpha, \beta)}{\partial(z, t)}, \end{aligned} \right\} \quad (3)$$

where $i = \sqrt{-1}$.

* 'Electromagnetic Theory,' vol. iii. p. 477 (1922); 'The Electrician,' Nov. 29, 1901.

† *Comptes Rendus*, cxlv. p. 417 (1907); *Rend. Lincei*, xviii. p. 83 (1909). The theory has been developed by the author in a number of papers. See, for instance, *Phil. Mag.* xxvi. p. 579 (1913); *Proc. London Math. Soc.* xviii. p. 95 (1919), xxi. p. 256 (1921).

Let the equation of the paraboloid be $r+x=a$, the origin being at the focus and r being the distance from the origin.

For the incident wave we write

$$\alpha = y - iz, \quad \beta = t - \frac{x}{c}, \quad f(\alpha, \beta) = F(\beta),$$

where $F(\beta)$ is real, the light being linearly polarized.

The reflected wave may be derived by means of the transformation *

$$x' = a - r, \quad t' = t, \quad y' = \frac{ay}{r+x}, \quad z' = \frac{az}{r+x},$$

which leaves points on the surface of the paraboloid unchanged. For this wave

$$\alpha = a \frac{y - iz}{r+x}, \quad \beta = t - \frac{a-r}{c}, \quad f(\alpha, \beta) = -F(\beta),$$

and it is easily seen that there is a singular ray $r+x=0$ for which E and H are infinite.

After passing through the focus this wave is presumably represented by

$$\alpha = a \frac{y - iz}{x-r}, \quad \beta = t - \frac{a+r}{c}, \quad f(\alpha, \beta) = +F(\beta),$$

and on a second reflexion at the surface of the paraboloid we obtain a plane wave represented by

$$\alpha = -\frac{a^2}{y+iz}, \quad \beta = t + \frac{x-2a}{c}, \quad f(\alpha, \beta) = -F(\beta).$$

This return wave has the axis of x as a singular ray, and electric dipoles, whose particular orientation in a transverse direction depends on the nature of the polarization, may be supposed to travel along the axis of x . We have, in fact,

$$E_x = 0, \quad E_y = \frac{a^2}{c} F(\beta) \frac{z^2 - y^2}{(y^2 + z^2)^2}, \quad E_z = -\frac{a^2}{c} F(\beta) \frac{2yz}{(y^2 + z^2)^2},$$

$$H_x = 0, \quad H_y = +E_z, \quad H_z = -E_y;$$

and it is seen that the lines of electric force in the plane of yz are those of an electric dipole at the origin whose axis is in the direction of the axis of y when $F(\beta)$ is negative. At a point on the axis of z close to the origin the direction of

* Proc. London Math. Soc. viii. p. 487 (1910).

the electric force is opposite to that of the polarization associated with the dipole.

By simply concentrating an electromagnetic field of a familiar type, we can in the limit, so to speak, create a type of electric dipole which travels with the velocity of light. It is true that the effect of diffraction has been eliminated by making the paraboloid extend to infinity, and it may be argued that with a paraboloid of finite size the true reflected wave would differ somewhat from the type imagined here in having no infinitely great concentration of energy; but as the paraboloid gets larger and larger, the effect of the diffracted light will presumably become small and the reflected wave tend more and more to the above type. There is still some uncertainty, however, regarding the correctness of this limiting solution from a physical standpoint, because we have four superposed fields some of which may exert forces on the moving electric dipoles associated with the others and produce some change. If this is the case, some type of field must be associated with the changes produced in the strength and motion of the electric dipoles, and our solution of the problem is incomplete. An interesting point arises here when we consider the state of affairs just before the passage to the limit. To obtain the limiting solution in which the moving electric dipoles are modified by the superposed fields, it seems necessary to assume that some change occurs when two electromagnetic fields of the ordinary type are superposed, and though generally negligibly small, it becomes quite marked when there is a concentration of energy in one or both of the fields.

This leads us to the conclusion that in general a secondary field is produced when the electromagnetic fields are superposed, and this may be the reason for the apparent failure of the classical theory to account for the properties of Bohr's hydrogen atom. The electron moves in the intense field of the nucleus, and no doubt a secondary field is produced when the fields of the electron and nucleus are superposed.

The existence of a secondary field may be necessary to maintain Newton's third law of motion. In the classical theory it is generally assumed that a field which accelerates an electron or proton is not directly modified although some change is produced in the field of the accelerated charge. It seems more natural to assume that the accelerating field receives a back kick and is in some way modified. Indeed, in Einstein's theory of light-quanta an atom is supposed to recoil when it emits a light-quantum in one direction, and is supposed to receive a kick when it absorbs a light-quantum.

There is one case in which no secondary field may be produced when two fields are superposed, and this is when the invariants $E^2 - H^2$ and (EH) for the total field are the sums of the corresponding invariants for the individual fields*. This is the case, for instance, when two fields of type (2) with different functions f and Ω are superposed, and it should be noticed that each field exerts no force on the electric charges associated with the other. The electric charges, in fact, move freely under no forces, and no forces are needed to keep them intact.

To obtain a radiant field with a finite amount of energy in a concentrated form, we may superpose a number of fields of type (2) so as to obtain something like a continuous volume distribution of electricity, or we may adopt some method of averaging similar to that adopted by Lorentz in his theory of a dielectric.

If the first method be adopted we still have expressions of type (2), but there is a volume density of electricity,

$$\rho = f\left(t - \frac{x}{c}\right) \left[\frac{\partial^2 \Omega}{\partial y^2} + \frac{\partial^2 \Omega}{\partial z^2} \right],$$

which moves in the direction of the axis of x with the velocity of light. The total energy is then finite if the integrals

$$\int_1 \left[\left(\frac{\partial \Omega}{\partial y} \right)^2 + \left(\frac{\partial \Omega}{\partial z} \right)^2 \right] dy dz = W$$

and

$$\int_{-\infty}^{\infty} \left[f\left(t - \frac{x}{c}\right) \right]^2 dx = I$$

are both finite. If, in particular †, we have

$$f\left(t - \frac{x}{c}\right) = \frac{\sin 2\pi\nu\left(t - \frac{x}{c}\right)}{t - \frac{x}{c}} = \int_0^{2\pi\nu} \cos p\left(t - \frac{x}{c}\right) dp,$$

the value of I is $2\pi^2\nu c$ and is proportional to ν .

* This criterion is suggested simply by the example and its invariance under a relativity transformation. It should, perhaps, be replaced by some other criterion, such as the additiveness of $E^2 - H^2$ alone or the absence of forces exerted by each individual field on the charges associated with the other.

† If this form of function does actually occur in the mathematical representation of a quantum, it seems to suggest that in the emission of a quantum an electron begins by performing small oscillations of frequency ν about the initial orbit. The oscillations get larger and larger, and finally die down when the electron reaches a state in which it is performing small oscillations of frequency ν about the final orbit.

A similar value is obtained by writing

$$f\left(t - \frac{x}{c}\right) = \frac{1 - \cos 2\pi\nu\left(t - \frac{x}{c}\right)}{t - \frac{x}{c}} = \int_0^{2\pi\nu} \sin p\left(t - \frac{x}{c}\right) dp.$$

In both cases there is a concentration of energy, and if W is regarded as a universal constant the total energy is proportional to ν , and we obtain a simple model of a light-quantum. To obtain a model of a quantum with circular polarization it is necessary to superpose two fields in which the dipoles are perpendicular, one field being of the first type and the other of the second type. The resulting field is then specified by vectors of type

$$H_x + iE_x = 0,$$

$$H_y + iE_y = i(H_z + iE_z) = \phi(y - iz) \int_0^{2\pi\nu} \frac{e^{\pm ip\left(t - \frac{x}{c}\right)}}{c} dp,$$

the $+$ sign referring to left-handed circular polarization and the $-$ sign to right-handed circular polarization.

An interesting point arises when an attempt is made to represent a linearly-polarized quantum for a limited portion of the wave-front by field components of type

$$E_x = H_x = E_y = H_y = 0, \quad E_y = H_z = A \frac{\sin 2\pi\nu\left(t - \frac{x}{c}\right)}{t - \frac{x}{c}}$$

where A is constant.

If such a quantum could pass without change of form through the electrostatic field of a condenser, say

$$E_x = E_z = 0, \quad E_y = E',$$

the total flow of energy across an area perpendicular to the axis of x would presumably be represented by

$$c \int_{-\infty}^{\infty} \left[A^2 \frac{\sin^2 2\pi\nu\left(t - \frac{x}{c}\right)}{\left(t - \frac{x}{c}\right)^2} + AE' \frac{\sin 2\pi\nu\left(t - \frac{x}{c}\right)}{t - \frac{x}{c}} \right] dt \\ = 2\pi^2\nu c A^2 + \pi c AE',$$

and is thus increased or decreased by the presence of the electrostatic field. It seems unlikely that this would actually occur, and it is more probable that the quantum is modified

in some way by the electrostatic field. In any case the effect of the field depends on the sign of A , and so is different for quanta of opposite phase. The effect may not occur in the case of radiations in which the time factor has an average value zero, and is, for instance,

$$\sin 2\pi\nu\left(t - \frac{x}{c}\right), \quad \cos 2\pi\nu\left(t - \frac{x}{c}\right), \quad \text{or} \quad \frac{1 - \cos 2\pi\nu\left(t - \frac{x}{c}\right)}{t - \frac{x}{c}},$$

the integration extending in the last case for a complete number of periods on each side of $t = \frac{x}{c}$.

If the method of averaging be adopted, it seems reasonable to specify the resultant field by means of an electric force E , an electric displacement D , a magnetic force H , and a magnet induction D , and to write *

$$\begin{aligned} E_x &= 0, & E_y &= \frac{\partial \Omega}{\partial y} f\left(t - \frac{x}{c}\right), & E_z &= \frac{\partial \Omega}{\partial z} f\left(t - \frac{x}{c}\right), \\ B_x &= 0, & B_y &= -\frac{\partial \Omega}{\partial z} f\left(t - \frac{x}{c}\right), & B_z &= \frac{\partial \Omega}{\partial y} f\left(t - \frac{x}{c}\right), \\ D_x &= 0, & D_y &= \frac{\partial \Gamma}{\partial z} f\left(t - \frac{x}{c}\right), & D_z &= -\frac{\partial \Gamma}{\partial y} f\left(t - \frac{x}{c}\right), \\ H_x &= 0, & H_y &= \frac{\partial \Gamma}{\partial y} f\left(t - \frac{x}{c}\right), & H_z &= \frac{\partial \Gamma}{\partial z} f\left(t - \frac{x}{c}\right), \end{aligned}$$

where Ω and Γ are functions of y and z . The equations

$$\begin{aligned} \text{curl } H &= \frac{1}{c} \frac{\partial D}{\partial t}, & \text{div. } D &= 0, \\ \text{curl } E &= -\frac{1}{c} \frac{\partial B}{\partial t}, & \text{div. } B &= 0 \end{aligned}$$

are then satisfied. If, moreover, the energy density is given by

$$\frac{1}{2}(ED) + \frac{1}{2}(BH) = \frac{\partial(\Omega, \Gamma)}{\partial(y, z)} \left[f\left(t - \frac{x}{c}\right) \right]^2,$$

and the flow of energy by

$$c(E_y H_z - E_z H_y) = c \frac{\partial(\Omega, \Gamma)}{\partial(y, z)} \left[f\left(t - \frac{x}{c}\right) \right]^2 = c(D_y B_z - D_z B_y),$$

* This type of field may be generalized by using expressions of type (3) for the components of $H + iE$ and similar expressions with a different a and f for the components of $B + iD$. In these expressions, β is the phase parameter and f need no longer be considered as a function of a and β , if there is a volume distribution of electricity.

energy and momentum again flow with the velocity of light, and a special form may be given to f , as before, to obtain a concentration of energy. The corresponding form of W is now

$$\iint \frac{\partial(\Omega, \Gamma)}{\partial(y, z)} dy dz = \iint d\Omega d\Gamma.$$

It is probable that the proposed expressions give us models of only some of the simplest forms of quanta, because when a quantum of one of these types is reflected obliquely at a moving mirror, a quantum radiation of another type is obtained.

If we use a field of type (3) to form a simple model of a quantum radiation, reflexion at a moving mirror is easily studied by means of a space-time transformation.

When the equation of the mirror is $x=ut$, an appropriate transformation is †

$$x^* = x - \frac{2c^2}{c^2 - u^2}(x - ut), \quad y^* = y;$$

$$t^* = t - \frac{2u}{c^2 - u^2}(x - ut), \quad z^* = z;$$

and we may put

$$\alpha^* = \alpha, \quad \beta^* = \beta, \quad f^*(\alpha^*, \beta^*) = -f(\alpha, \beta).$$

There is, however, some uncertainty as to the correctness of this analysis, because there may be an interaction between the incident and reflected field with the formation of a secondary field. The analysis may, however, be supposed to give us a first approximation.

When the incident field is of type (2), we have

$$\alpha = \Omega(y, z) + i\Lambda(y, z), \quad \beta = ct - x, \quad f(\alpha, \beta) = f\left(t - \frac{x}{c}\right),$$

$$\alpha^* = \alpha, \quad \beta^* = \frac{(t^* + x^*)(c + u)}{c - u}.$$

Hence, if
$$f\left(t - \frac{x}{c}\right) = \frac{\sin 2\pi\nu\left(t - \frac{x}{c}\right)}{t - \frac{x}{c}},$$

the reflected field is of the same type, but its frequency is

$$\nu^* = \nu \frac{c + u}{c - u},$$

† Phil. Mag. xviii. p. 894 (1909), xix. (May 1910). Bull. Nat. Research Council, vol. iv. no. 24, p. 109 (1922).

in accordance with Doppler's principle. It is quite possible, of course, that when the incidence is oblique, the secondary field is of such a nature that effectively the reflected quantum radiation is still of the simple type (2). This question of the interaction between fields is a difficult one; some light may be shed upon it, however, by the recent researches of A. H. Compton and W. Duane.

A slight indication of the nature of the interaction may, perhaps, be obtained by a slight modification of Whittaker's quantum mechanism in the atom.

An essential feature of Whittaker's quantum mechanism is that something analogous to a magnetic current or an electric shell is induced by the magnetic field of an approaching electron.

The secondary field of an electron and a proton may provide such a mechanism, especially if it contains entities analogous to electric dipoles travelling with the velocity of light: for these may be orientated under the action of the magnetic field, so that they tend to set themselves more nearly parallel to the electron's line of motion, and thus produce a force retarding the electron*.

The dipoles in the secondary field may be regarded as analogous to eddies. This analogy may, perhaps, be made a little clearer by considering the diffraction of light by a black screen, on the supposition that a type of radiation from the edge of the screen is superposed upon the direct light or darkness obtained by the methods of geometrical optics. This supposition is in some respects analogous to the hypothesis of inflected rays adopted by Young in his Theory of Diffraction†, but the radiation issuing from the edge of the screen seems to be composed of elementary radiations with singular rays consisting of entities analogous to electric dipoles moving along straight lines with the velocity of light. There is an elementary radiation of this type for each element of the edge, and the infinite values of the light-vectors disappear on integration, leaving only finite discontinuities just sufficient to balance those introduced by the methods of geometrical optics. The solution of the mathematical problem has been discussed in detail by F. Kottler‡,

* If the atomic electron's field is regarded to a first approximation as of type (1), the dipoles radiated in the plane of the electron's orbit will initially have their axes in this plane. The field of the approaching electron will tend to swing them out of this plane.

† See R. W. Wood's 'Physical Optics,' p. 183.

‡ *Wiener Berichte*, cxxix. p. 1 (1920); *Ann. d. Phys.* lxx. p. 405 (1923). The method was proposed also by the author, and illustrated by an example taken from the theory of sound: 'Electrical and Optical Wave Motion,' Ch. V.

who regards it as an indication that radiation with a concentration of energy has a physical existence. Kottler illustrates the theory by a simple example based on Kirchhoff's treatment of diffraction which he regards as quite rigorous in the case of a black screen.

Treating the light as unpolarized, he specifies it by a scalar quantity Aue^{ikrt} , where A and k are constants. For the incident light $u = u_0 = \frac{1}{r} e^{-ikr}$, where r is the distance from the source. For the total light Kirchhoff's formula gives

$$\begin{aligned} u &= u_0 + \frac{1}{4\pi} \int dS \left[u_0 \frac{\partial}{\partial n} \left(\frac{1}{R} e^{-ikR} \right) - \frac{\partial u_0}{\partial n} \frac{1}{R} e^{-ikR} \right] \\ &= u_0 + \frac{1}{4\pi} \int dS \operatorname{rot}_n \left\{ \frac{1}{rR} e^{-ik(r+R)} \frac{[rR]}{rR + (rR)} \right\}, \end{aligned}$$

where the integration extends over the illuminated part of the screen and the suffix n denotes that we must take the component of $\operatorname{rot} \{ \}$ along the outward normal to the surface. The vectors r and R are drawn radially from the source, and P to a point on the black surface.

Kottler transforms the integral into a line integral round the boundary of the illuminated portion of the screen (*i. e.*, the edge when the screen has a sharp edge). In applying Stokes's theorem a separate treatment must be given of the case in which the line joining P to the source meets the illuminated portion of the screen. In this case it is convenient to use the equivalent formula

$$\begin{aligned} u &= -\frac{1}{4\pi} \int dS \left[u_0 \frac{\partial}{\partial n} \left(\frac{1}{R} e^{-ikR} \right) - \frac{\partial u_0}{\partial n} \frac{1}{R} e^{-ikR} \right] \\ &= -\frac{1}{4\pi} \int dS \operatorname{rot}_n \left\{ \frac{1}{rR} e^{-ik(r+R)} \frac{[rR]}{rR + (rR)} \right\}, \end{aligned}$$

taken over a surface which has the same boundary as the illuminated portion of the screen, and together with it forms a complete barrier to the incident light. Kottler finds that in both cases *

$$u = \{u_0\} + \frac{1}{4\pi} \int [rR]_s ds \frac{e^{-ik(r+R)}}{rR \{rR + (rR)\}},$$

where $[rR]_s$ denotes the component of the vector product $[rR]$ in the direction of the line element ds . The term $\{u_0\}$

* See also G. A. Maggi, *Ann. di. Mat.* xvi. p. 37 (1888). The transformation indicates the relation between the ideas of Young and Fresnel.

represents light obtained by the methods of geometrical optics, and is thus zero inside the geometrical shadow and equal to u_0 outside. The light diffracted from the edge of the screen has singular rays because the integrand becomes infinite when the line joining the source to P meets the edge of the screen before it reaches P.

The analogy between diffraction by a black screen and the flow of a fluid round an obstacle may be quite close. In the hydrodynamical problem a first approximation to the solution is obtained by using the method of discontinuous flow, and the surface of discontinuity may be regarded as analogous to the boundary of the geometrical shadow. To obtain a second approximation we must regard the surface of discontinuity as surrounded by a region of eddy motion, and the optical analogue of the eddy seems to be the electric dipole.

It is rather significant that the singular rays appear when the diffraction problem is solved by means of a simple integral instead of a double integral. This may be compared with the fact that in addition to the very general solution of the wave-equation expressed by Whittaker and Watson in the form of a double integral

$$V = \int_0^\pi \int_0^{2\pi} F(x \sin \alpha \cos \beta + y \sin \alpha \sin \beta + z \cos \alpha - ct, \alpha, \beta) d\alpha d\beta$$

there is also a very general solution in the form of a simple integral *

$$V = \int_0^{2\pi} f(x \cos \theta + y \sin \theta - ct, x \sin \theta - y \cos \theta - iz, \theta) d\theta,$$

in which each element of the integral generally represents a wave-function with singular rays. The transition from one form to the other can, no doubt, be made in many ways. One transformation is provided by the integral formula

$$\begin{aligned} & e^{ik(x \sin \alpha \cos \beta + y \sin \alpha \sin \beta + z \cos \alpha - ct)} \\ &= \frac{1}{2\pi} \int_0^{2\pi} \frac{e^{ik[x \cos \theta + y \sin \theta - ct + i \cos \alpha (x \sin \theta - y \cos \theta - iz)]}}{1 - \tan \frac{\alpha}{2} \cdot e^{i(\beta - \theta)}} d\theta, \end{aligned}$$

which is easily proved with the aid of Cauchy's theorem. In this case the singular rays are at infinity, and the wave-function represented by the integral has no discontinuities in finite regions of space.

* This is only one of a large class of definite integral solutions obtained by generalizing fields of type (3). See Bull. National Research Council, iv. no. 24, p. 144 (1922).

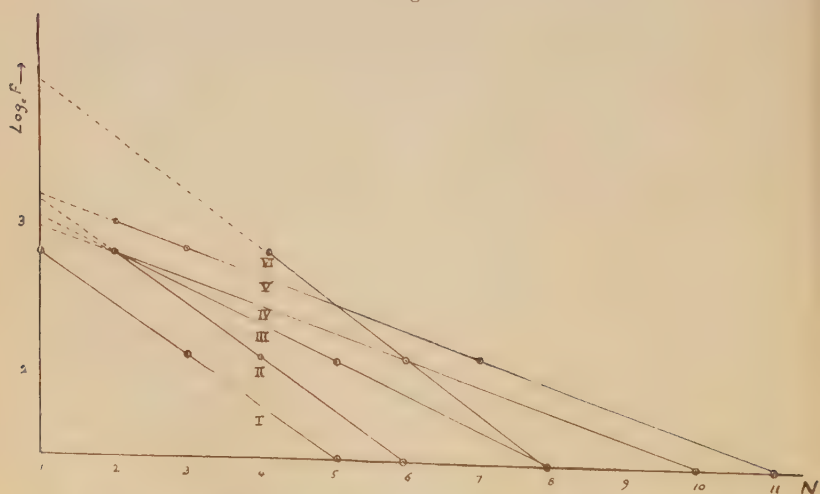
CVIII. *Some further Observations on the Relation between the Focal Length of Microscope Objectives and the Number of Fringes seen in Convergent Polarized Light.* By F. IAN G. RAWLINS*.

THE object of the present paper is to describe a further series of experiments on the relationship which exists between the number of interference rings which are seen in crystal sections (cut in various directions) in convergent polarized light by means of a microscope.

The first series of readings already described by the author† referred only to crystalline plates cut perpendicularly to the optic axis in the case of uni-axial crystals, and perpendicularly to the acute bisectrix for bi-axial crystals.

In the case now under consideration, however, sections cut at various orientations were investigated, and in every instance, as shown by the graph, the equation $F = F_0 e^{-AN}$ is satisfied.

Fig. 1.



F is the focal length of the objectives in millimetres, N is the number of rings observed, while A is a parameter which is easily seen to be given by the expression $A = \frac{d \log_e F}{dN}$. The numerical values of A are given in the table, together with the experimental data and the orientations.

* Communicated by the Author.

† Phil. Mag. xliii. p. 766 (April 1922).

The apparatus was substantially the same as that already described*, except that the Wratten filter was abolished and the observations made by sodium light. The same sub-stage, condenser, tube-length, eyepiece, and Becké lens have been used throughout.

Considerable interest centres round the physical significance of the constant A . It will be noticed from the graph how there is a tendency for the lines representing the family $\log_e F = \log_e F_0 - AN$ to fall into parallel groups. Thus the curves I, II, and VI are parallel, as are also IV and V. Experiments are contemplated to investigate this more closely, the results of which it is hoped may be communicated later. Meanwhile, the validity of the original exponential expression is considerably extended.

Number on graph.	I	II	III	IV	V	VI
Mineral	Tourmaline.	Quartz.	Barytes.	Barytes.	Topaz.	Topaz.
Orientation	optic axis.	optic axis.	⊥ one optic axis.	⊥ obtuse bisectrix.	⊥ one optic axis.	one optic axis.
Thickness in mm.	1.60	2.00	2.40	3.00	1.35	0.50
$A = \tan \alpha$ $\frac{d \log_e F}{dN}$.1853	.3640	.2217	.3640	.1853	.3640
Objective's focal length = F mm.	Number of Rings N .					
4	5	6	8	10	11	8
8	3	4	5	6	7	6
16	1	2	2	2	3	4
22	2	...

In conclusion, the author wishes to express his obligations to Mr. C. W. Hawksley for his help with the apparatus, and also to Mr. G. W. Brown for his skill in the preparation of material.

* *Loc. cit.*

CIV. *The Emission of Secondary Electrons from Metals under Electronic Bombardment.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN the *Philosophical Magazine* for May 1923, I gave an account of the secondary emission obtained from the nickel plate of a three-electrode valve, and criticized some conclusions arrived at by Prof. Horton and Dr. Davies in somewhat similar investigations.

In the experiments on secondary emission the electrons from a hot filament in a gas-free valve move towards a grid whose potential is V_G above the filament, and a proportion of the electrons pass through the grid and strike the plate whose potential is V_P above the filament.

The plate current was measured for various values of the potential V_P , V_G being kept constant, and the curves obtained are reproduced here in figs. 1 and 2.

The main feature of the curves is the fact that over a considerable range of values of V_P the current decreases as V_P increases, which is of course due to secondary emission. The details of the curves however, such as the points at which the plate current attains its maxima and minimum values, appear to me to depend on the grid; but Prof. Horton and Dr. Davies in a recent communication * maintain that their results cannot be subject to variations depending on the grid, as they used a grid of very fine mesh.

The use of grids is now very common, particularly in work on ionizing and radiating potentials, and it seems therefore worth while to discuss more fully how far the fineness of the grid can avoid the difficulties which I pointed out.

The peculiarity of the curves in fig. 1 is that, although the secondary emission or reflexion depend upon the velocity of impact on the plate, that is on V_P and not on V_G , the curves are entirely different for different values of V_G . It is not therefore possible to deduce directly from the shape of a curve accurate information about secondary emission, as there must be another factor which influences this shape.

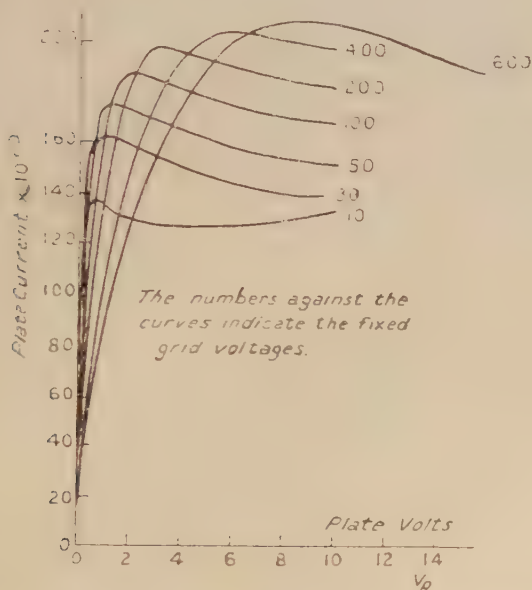
Prof. Horton and Dr. Davies used only one value of V_G , and deduced from a bend in their curve that secondary emission commenced for a velocity of impact corresponding to a potential drop of about 10 volts.

In my previous paper, I pointed out that the differences

* *Phil. Mag.* July 1923, p. 129.

between the curves in fig. 1 were accounted for by the bending of the paths of the electrons which passed close to the grid wires. Bending occurs whatever the size of the grid wires and spaces, and the application of a magnetic field, which causes the electrons to move in spirals, will not eliminate its effects: and there is therefore no reason to suppose that, if Prof. Horton and Dr. Davies had used a different value of V_g , their bend would have occurred at the same place. They do not, however, appear to claim that their grid produced no deviation of the electrons, but they

Fig. 1.



still claim that the sharpness of the bend between the points F and G on their figure (Phil. Mag. July, p. 130, 1923) indicates the commencement of a new effect.

This bend occurs at the tenth point on their curve (counting from the left). A bend of equal sharpness is found at the twelfth point, but as they attributed no significance to the latter point, the writer assumed it could be accounted for by experimental error. An equal error of about 1.7 per cent. would, however, dispose of the sharpness of the bend at the tenth point on which their conclusions are based.

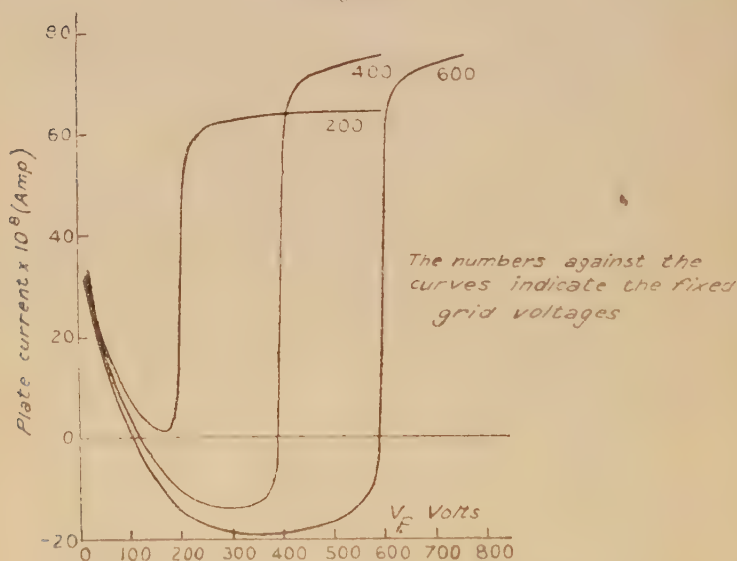
Those who are familiar with the use of the electrometer for the measurement of small currents and the difficulty of

keeping a steady, small emission from a filament, have reason to hesitate before accepting as evidence for important physical phenomena the result of experiments depending on the absence of an error of the order of 1·7 per cent.

The final rise of the curves (fig. 2) involves the question of how far the grid can be regarded as a shield.

This rise commences before V_P reaches the same value as V_G , and in this connexion the writer pointed out that the field near the plate actually did reverse before V_P reached the value V_G .

Fig. 2.



The writer is glad now that Prof. Horton and Dr. Davies have given the dimensions of their grid, to agree that in their experiments the electric force near the plate does not change sign until the grid is at nearly the same potential as the plate. But he cannot agree with them when they say that the phenomenon presents no difficulty of interpretation.

In their experiments secondary electrons begin to return to the plate when a field of about 5 volts is attracting them to the grid, which they attribute partly to a small voltage being necessary for saturation and partly to some of the secondary electrons being given off in holes of molecular dimensions in the plate.

An explanation involving this last assumption can scarcely be said to present no difficulty.

The plate current continues to increase as V_P is made larger than V_G , and Prof. Horton and Dr. Davies found that their current reached a saturation value when $V_P - V_G = 9$ volts, interpreted as indicating that the maximum velocity of emission of the secondaries was equivalent to 9 volts. In my curves (fig. 2) I did not get a very definite saturation, and pointed out that the sharpness of the final bend was obscured owing to the fact that as V_P was increased, electrons which originally went direct to the grid from the filament were diverted to the plate.

Prof. Horton and Dr. Davies say on this point: "The proof that the shielding action of the grid was almost perfect disposes of Mr. Gill's contention that because no allowance was made for an increase with increasing plate potential of the primary current to the plate at the expense of the primary current to the grid the estimate of 9 volts. . . . is unreliable."

This statement involves a complete misapprehension of the effect of the grid. All that was shown by Dr. Appleton (to whom they refer) was that at the surface of the plate the shielding of their grid was nearly perfect. The question of whether an electron from the filament goes direct to the grid, or passes through it, has nothing whatever to do with the field at the surface of the plate, but is largely determined by the field in the neighbourhood of the grid wires.

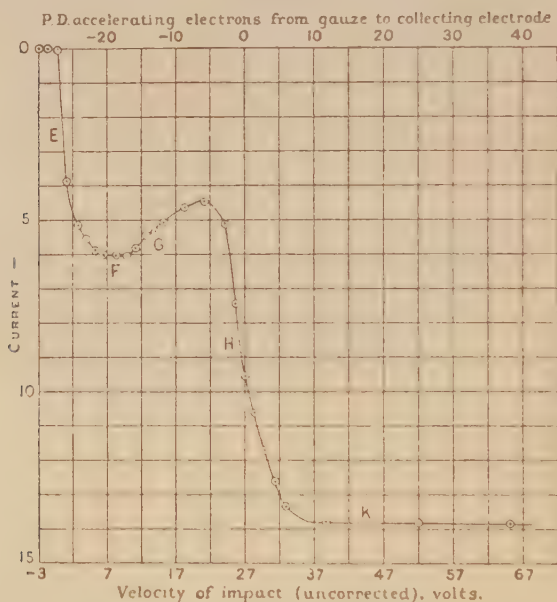
The phrase "shielding action of the grid" appears to be an unfortunate one, as implying that the field everywhere between the grid and the plate is determined solely by their potentials and not by that of the filament. What actually happens is that near the plate and up to a certain distance from the grid the field is determined very accurately by the potentials of grid and plate alone, and with the finer grid this is true over a larger space than with the more open type; but near the grid the field is influenced by the potential of the filament, and, as I pointed out in my original paper, the plane of the grid is not an equipotential surface. The potential at the centre of the grid spaces may, if the wires are thin, differ considerably from that of the grid wires owing to the large force just outside such a wire.

The above statement of Prof. Horton and Dr. Davies appears to imply that as the plate potential is increased, none of the primary current to the grid is diverted to the plate, since they say that my contention that this occurs is disposed of. This is equivalent to asserting that the number of electrons from the filament which passes through the grid

is constant so far as variation of the plate potential is concerned. If this supposition is taken as being correct and applied to their own curve, it leads to conclusions which are very difficult to accept.

Their curve (Phil. Mag. July, p. 130, 1923) (reproduced in fig. 3 *) shows that the total current passing through the grid is 13.8 units about, this being their measure of the plate current for $V_p = 36$ and upwards when no electrons return from the plate to the grid.

Fig 3.



For $V_p = 7$ the plate current is 6 units, and on the assumption that 13.8 units pass through the grid, since all of these reach the plate, the conclusion is that for 138 electrons hitting the plate 138—60 are returned to the grid by reflexion or secondary emission—*i. e.*, for a velocity of impact of only 7 volts we get a secondary emission and a reflexion of more than 50 per cent.

If the same reasoning be applied to the earlier portion of the curve, the result is still more surprising, and appears to indicate that as the velocity of impact is reduced *below* the equivalent of 7 volts the secondary emission (or reflexion) increases, while a consideration of the flat portion at F indicates that from 7 to 10 volts the secondary emission remains the same.

* Their current ordinate is measured in the opposite direction to mine.

I do not think it can possibly be maintained that, if the field on one side of a grid is altered, the number of electrons which pass through will remain the same.

The chief conclusions about grids appear to be therefore:—

(1) It is difficult to find what proportion of the current from the filament passes through them.

(2) The electrons after passing through do not in general continue to move at right angles to the grid.

(3) The field between the grid and the next electrode is not everywhere independent of the potential of any other electrodes.

(4) The plane of the grid is not an equipotential surface, and the electrons passing through have different velocities.

The use of a very fine grid removes to some extent the difficulty (3), but does not necessarily get over the other three.

In addition, though this has not been discussed, there is sometimes the further complication of reflexion or secondary emission from the grid.

Yours faithfully,

Merton College,
Oxford.

E. W. B. GILL.

CV. *On the Adiabatic and Isothermal Piezo-Electric Constants of Tourmaline.* By DAVID A. KEYS, M.A., Ph.D.*

THE question of any large difference in the piezo-electric constant of tourmaline, when compressed adiabatically and isothermally, is one of the greatest importance in making measurements by the piezo-electric method †. In general, the crystal vessel is calibrated by applying static pressures to the crystals and finding the effect produced. The calibration pressures will necessarily be applied relatively slowly as compared with the time taken for the pressure in an explosive wave to reach its maximum. Thus the crystals are calibrated isothermally and used adiabatically. Any difference in the piezo-electric constant in the two cases will cause an error in calibration.

The experimental determination of the difference between

* Communicated by the Author.

† Phil. Mag. vol. xlii. p. 473 (1921).

the adiabatic and isothermal effects is so difficult to carry out, that it seemed expedient to calculate thermodynamically the difference to be expected. This may be done as follows:—

Let one gram of the tourmaline be given a quantity of heat dQ . Then if T is the absolute temperature and dS the change in entropy, we have

$$\begin{aligned} dQ &= T \cdot dS \\ &= T \left(\frac{\partial S}{\partial T} \right)_p dT + T \left(\frac{\partial S}{\partial P} \right)_T dP \\ &= C_p dT - T \left(\frac{\partial v}{\partial T} \right)_p dP, \end{aligned}$$

because

$$\left(\frac{\partial S}{\partial T} \right)_p = \frac{C_p}{T}$$

and

$$\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial v}{\partial T} \right)_p.$$

In the case of solids, $\frac{\partial v}{\partial T} = \alpha v_0$ where α = coefficient of cubical expansion and v_0 = volume of the gramme of tourmaline at 0°C .

Hence for an adiabatic change we have $dQ=0$, and therefore

$$C_p dT = T \left(\frac{\partial v}{\partial T} \right)_p \cdot dP = T \alpha v_0 dP$$

or

$$dT = \frac{T \alpha v_0}{C_p} \cdot dP.$$

Suppose the pressure suddenly increases by an amount P dynes. Then the consequent change in temperature will be

$$\Delta T = \frac{T \alpha v_0 P}{C_p} \quad \dots \quad (1)$$

Now, considering one gramme of tourmaline, $v_0 = \frac{1}{d}$ where d = density of tourmaline at 0°C . Thus (1) becomes

$$\Delta T = \frac{T \alpha P}{C_p \cdot d} \quad \dots \quad (2)$$

When $T = 17^{\circ} \text{C.} = 220^{\circ} \text{abs.},$

$$\alpha = 13.89 \times 10^{-6} *,$$

$$d = 3.15 \dagger,$$

$$C_p = 0.200 \text{ calories per gm.} = 0.84 \times 10^7 \text{ ergs per gm.} \ddagger ;$$

$$\therefore \Delta T = 1.52 \times 10^{-10} \text{ P in degrees centigrade.}$$

If $P = 100 \text{ atmospheres} = 10^8 \text{ dynes, then}$

$$\Delta T = .0152^{\circ} \text{C.}$$

Owing to this change in temperature, we shall have a pyro-electric charge produced. The pyro-electric constant of tourmaline is 1.2 e.s. units per cm.^2 per degree centigrade §. Hence the charge produced by this rise in temperature

$$= .018 \text{ e.s. units per cm.}^2$$

The piezo-electric charge produced by 100 atmospheres is

$$= 5.4 \times 10^{-8} \times 10^8 = 5.4 \text{ e.s. units per cm.}^2 \parallel$$

The resulting charge would be

$$= 5.4 - .018 = 5.382 \text{ e.s. units per cm.}^2$$

Hence the difference between the adiabatic and isothermal piezo-electric constants of tourmaline is only about 0.33 per cent. Consequently there is only a very slight error caused by calibrating the crystals isothermally and using them adiabatically.

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McGill University.

* Voigt, *Kristallphysik*, p. 293.

† Landolt-Börnstein Tables.

‡ Abraham & Sacerdote, *Recueil de Constantes Physiques*, p. 311.

§ Poynting & Thomson, 'Electricity and Magnetism', p. 153.

|| Poynting & Thomson, 'Electricity and Magnetism', p. 160; also Curie, *Œuvres*, p. 23.

CVI. *Space.**By* NORMAN CAMPBELL, *Sc.D.***Summary.*

IT is inquired what is the connexion of the conception of "space" with the experimental geometry which was discussed in a previous paper. It is concluded that space, though based on the experimental concept "position," which is a typical pure derived magnitude, is itself a hypothetical idea and involved in theories rather than in laws. A brief and very summary outline of the theory of space, as it appears in classical physics, is given, and a few remarks offered on the alterations of this theory that are rendered necessary by the general theory of relativity.

1. In a previous paper† I discussed what laws were necessary in order that the three fundamental geometric magnitudes—length, angle, and area—should be measurable. It was concluded (1) that these magnitudes were similar to all other fundamental magnitudes in requiring for their measurement the laws of equality and addition; (2) that the conditions in which these laws are true are those which describe rigid bodies, and that, consequently, the only sound definition of a rigid body is one for which these laws are true; (3) that, from the fact that the laws are true and that these magnitudes are measurable, we can deduce a number of propositions, corresponding roughly to the contents of Books I., II., III., VI. of Euclid's Elements; (4) that the axioms on which those books are based correspond somewhat closely to statements of the necessary laws of measurement, and the proofs there given to those by which these propositions can be proved from these laws. The precise significance of the correspondence (4) will be estimated differently by different persons; the questions which it raises are personal and historical rather than scientific. But to me, at least, it seems sufficiently significant to justify the use of the term "geometry," or "experimental geometry," to describe the branch of physics which is concerned with the fundamental measurement of these magnitudes, and therefore with the properties common to all rigid bodies.

But geometry in this sense has nothing to do with space; and it is largely in order to draw attention to this fact that

* Communicated by the Author.

† Phil. Mag. vol. xlv. p. 15 (1922).

I urge that the term is appropriate. For geometry is sometimes said to consist in the study of space; and here is a branch of science, at least closely allied to it, in which that conception finds no place whatever. The question therefore arises, what is the relation of the conception of space to experimental geometry? Is it a conception belonging to experimental science at all, or is it purely mathematical or philosophical? And, if it does belong to experimental science, is it a concept or a hypothetical idea *? These are the questions which will be discussed in this paper.

2. Space is closely associated with position. Position takes its pre-scientific origin from relations instinctively recognized. The position of an object is connected, as Poincaré has pointed out, with the muscular movements necessary to bring it within the range of perception, visual or tactual. Two small objects, or points, have the same position if they are coincident, and therefore, by the meaning of coincidence, are attained by the same muscular movements. The identity of "visual" and "tactual" space arises from the important fact that points which are coincident for all observers, in respect of the movements that control visual perceptions, are also coincident in respect of those which control tactual perceptions.

Since they are based on primary sensations of the same kind, the crude conception of position and the crude conceptions of geometric magnitudes are closely connected. But it is important to insist that position, in its original meaning, is quite independent of the idea of a rigid body; objects have position even if they are not rigid bodies or parts of them; in deed, since one of the most important applications of the conception of position is to the interpretation of those changes which we call motion, and since such changes are inevitably associated with some absence of rigidity, it might be urged that the study of position and the study of rigid bodies were diametrically opposed. The close connexion between them in science arises only when an attempt is made to convert position from a crude to a scientific conception by measurement.

In order to measure position, we must find some method of assigning numerals to objects in such a way that identity of numerals denotes contiguity and diversity of numerals separation. Further, since we have some crude appreciation of magnitude of separation based on muscular sensation, it

* These terms and many others employed here, such as derived and fundamental magnitude, numerical law, law of measurement, and so on, are used in the sense carefully defined in my 'Physics.'

is desirable that, in general, greater diversity of numerals shall correspond to greater separation. It is impossible to measure position as a fundamental magnitude (for two similar positions cannot be combined to give a third position different from either); it must be measured as derived, and the numerals to be assigned must be those denoting magnitudes of some other kind. The magnitudes that are used for this purpose are the geometric magnitudes which are characteristic of rigid bodies and were discussed in the preceding paper, *i. e.*, length, angle, and area. Probably these are the only magnitudes that can actually be used; but it must be noted that it is just conceivable that this limitation might not have existed. It is not impossible (to speak in terms of our present conceptions) that every point in space might have a different temperature: if that were so, position might be identified and measured by temperature. Or, if it is held that denotation by a single one-dimensional magnitude is inconsistent with a three-dimensional space, it might have been possible to use three magnitudes of different kinds, such as temperature, gravitational force, and electric potential. The association of the conception of position, and thence of space, with the geometric magnitudes may be an actual fact of the world as it exists, but it is not certainly inherent in the meaning of those conceptions. If there is any necessary association of space with the properties of rigid bodies, it arises rather from the fact that, when the most accurate measurements are to be made, points forming parts of the surface of rigid bodies are the only objects having position.

3. Position, then, is a derived magnitude measured by the fundamental geometric magnitudes, just as density (the magnitude connected with flotation) is measured by mass and volume, although, in its original meaning, it has nothing to do with those magnitudes. We proceed to ask what are the laws upon which this system of derived measurement depends.

Consider, first, the system in which position is fixed entirely by "distances." By the distance between two points we mean, in the first instance, the length of the straight line the ends of which are coincident with those points—that is a mere verbal definition. We take a number of points on the surface of some one rigid body and attempt to measure the position of other points from these points, which form the frame of reference. We immediately find that, whatever points of reference we choose, there are many points of which we want to measure the position, but which have no distance from some or all of the points of reference, because (owing

to the intervention of solid bodies, as we say now) we cannot place a straight line between the measured point and the points of reference. Measurement by any such system is made possible only by changing somewhat the meaning of distance. We permit the use of calipers, and propose to say that the distance of A from B is d , if two points on some rigid body can be brought into coincidence, first with A and B, and then with the ends of a straight line of length d . This change in the meaning of distance converts the conception into a definite concept, implying the truth of a law, namely that the distance determined by means of calipers is the same whatever the form of the calipers, so long as they are rigid. This is the first law involved in the measurement of position.

Having thus made possible the measurement of the distance between any point and the points of reference, we proceed to inquire whether the necessary condition can be fulfilled, that points are coincident and have the same position if, and only if, their distances from the points of reference are the same. It turns out that it is fulfilled if we choose at least four points of reference not lying in the same plane, and regard position as determined by the set of values of all these four or more distances. The second law of measurement is, therefore, that two points are coincident if, and only if, their distances from each of four or more non-coplanar points are the same. The third law, not of much importance for our present purpose, is that, if n points of reference are chosen, of which no four lie in a plane, there are $n-3$ numerical laws relating the n distances of any point from the points of reference and the distances between those points.

The systems of "coordinates" more usually employed for fixing position, such as the Cartesian or the Eulerian, involve angles as well as distances. The nature of the calipers which such systems involve is much more complicated, but there is again a law corresponding to the first given above. To the second, of course, corresponds the law that three coordinates fix the point, while there is no law corresponding to the third; the coordinates are independent. The recognition of alternative systems of coordinates and of measuring position requires the knowledge of further laws describing their equivalence; if the position of a point measured with one system of coordinates relative to one frame of reference is known, numerical laws must be available to determine its position measured with another system relative to another frame, the positions of the points constituting one frame relative to those constituting another being known. Of

course, it is unnecessary here to state these relations, but attention should be drawn to the law that there are such general relations, and that the position of a point can be determined relative to *any* frame of reference by means of the coordinates appropriate to the form of that frame.

4. It must now be asked whether these laws, which make possible the measurement of position as a derived magnitude, are geometric laws, belonging to the study of rigid bodies and deducible from the fact that there are measurable geometric magnitudes, or whether they are new laws independent of that study. The second law, namely, that on which is based—in some manner that we have yet to discuss—the statement that space is three-dimensional, is clearly a new law; there is nothing whatever in the laws which determine the measurement of lengths and angles to tell us how many lengths and angles, based on any frame of reference, are necessary to fix a point. The first law, on the other hand, may seem at first sight to be nothing but a special case of the law of equality for lengths and angles—namely, that the relation of equality is transitive and symmetrical. But a little inquiry will show that something more is involved; it is the proposition that we might express now by saying that the distance between two points is not altered by the mere intervention of a solid obstacle. For, with our present conceptions, it is conceivable that all calipers might be changed in the same way by the insertion of various bodies between their tips, the change depending on the body inserted. The manner in which we have defined distance, involving the use of calipers, makes that expression and suggestion meaningless; the only way in which we can state the law is by the assertion that all propositions which are true of distances that can be measured directly by the introduction of a straight line are true also of distances that have to be measured indirectly by means of calipers—together with a similar assertion for angles. That is an extremely important proposition, which is not a mere consequence of the law of equality.

Similarly with the laws asserting equivalence of different systems of measurement. It is true that the relation between the Cartesian coordinates of a point on a cube, referred to the faces of a cube meeting at a corner, and the tetrahedral coordinates, referred to the four corners in which those faces meet, must follow from the geometry of the cube, this geometry being a consequence of the laws of measurement of the magnitudes and of the existence of cubes. But the fact that we can cut away most of the cube in any manner,

leaving enough to support the point and frame of reference, and still find the same relation to hold—that fact is new and not implied in solid geometry as we interpret it. If it is true, as we might say now, that “space is not distorted by the presence of matter in it,” that is a law which can only be established by experiment; it might be untrue and yet, so far as we can see, the laws of geometry, asserting the properties of rigid bodies, might yet remain unaltered.

5. Position then is a magnitude derived, like other derived magnitudes, from laws, some of which are numerical, some not. These laws include the geometric laws, but include also others which are distinctive laws of position. Position differs from all other derived magnitudes (I believe) because it is not a constant in the numerical laws on which it is based: it differs from most, if not all, others, because positions cannot be arranged in a one-dimensional series; otherwise it resembles them.

Now let us turn to space. If the aether is the subject of the verb to undulate, then space is the object of the verb to occupy. In experimental science space is that which is occupied by matter. The conception arises from a contemplation of the positions which actually occur. Let us examine any collection of rigid bodies, including the frame of reference, surrounded by air. If all these bodies are at relative rest (that is to say, the distance between every pair of points remains unaltered during the examination); and if we measure the positions of all the points we can define in such a system; then we shall find that only a very small proportion of the positions possible according to our system of measurement actually occur; we do not even find all values within a given range in all possible combinations. (It must be remembered that, in virtue of the step in fundamental measurement, the number of values is finite.) If we permit ourselves to introduce new rigid bodies, still leaving the old ones fixed, we can add very considerably to the number of positions that we can measure; but however many we introduce there will be some that cannot be measured. These missing positions may appear, however, if we change the relative positions of the original bodies. With any set of bodies we can discover rules, very complicated it may be, relating the positions that do occur (Class A) to those which can be made to occur (Class B) and those that cannot be made to occur (Class C). There is a certain complicated sense in which members of Class B and of Class C lie numerically between pairs of members of Class A, and this sense is rather different for Classes B and C. But

it is unnecessary to elaborate. Such facts as these, universally known, but immensely tedious to state formally, lead us to the idea that there are potential positions corresponding to all possible values of the coordinates, but that those of Class C are occupied by matter, those of Class B are not occupied at all, while Class A are those which lie on the boundary between occupied and unoccupied regions.

But what can be meant by a potential position which is not an actual position? If position is a measurable magnitude, anything that is not measurable is not a position. For it is no mere accidental limitation which prevents us from measuring positions occupied by a solid body; if there were no solid bodies which prevented us from measuring certain positions there would be no fundamental magnitudes by means of which we could measure them. The facts which distinguish potential and actual positions are facts inextricably involved in the concept position. Potential position is not therefore a concept; if it has any meaning for experimental science, it must be a hypothetical idea and any proposition in which it is involved must be a theory*.

6. Let us then attempt to state in outline a theory by means of an "hypothesis" and "dictionary," the two parts of which, as I have concluded in a full discussion of the matter, every theory must consist. The hypothesis must state the properties of space. It consists of two parts. The first, concerned with the properties of pure space, is the set of propositions elaborated in any treatise on analytical metrical geometry. For the time being, we will suppose that the hypothetical space is three-dimensional and Euclidean. The conception of an infinite three-dimensional continuum of points is introduced, each point being a set of values of each of the three coordinates. Lines, surfaces, and spaces or regions are defined as collections of points between the coordinates of which certain analytical relations exist; distances between points, lengths of lines, areas of surfaces, and volumes of regions are defined as certain functions of these related coordinates. These and other similar definitions are shown to be mutually consistent, and from them are deduced by mathematical reasoning the whole series of propositions. The second part states the relation between space and matter: the most fundamental proposition, and the

* Perhaps it will be well to explain once more that by "hypothetical" and "theory" I do not attach the slightest connotation of doubt. Some hypothetical ideas seem to me more obviously valid and some theories more obviously true than any concepts or laws.

only one involved in the simplest theory of space, is that space can be occupied by matter.

The dictionary connects these hypothetical ideas (points, related sets of points, and occupation by matter) with experimental concepts. It states that the proposition that space is occupied by matter means that there are positions of Class A, measurable and distinguishable from those of Classes B and C which are not measurable. In order to translate propositions asserting that certain specified points (and not merely some points) are occupied, it is necessary to introduce the frame of reference, and consequently the full entry in the dictionary becomes very elaborate. But, roughly, it states that, when it is said that certain points P are occupied and others Q are not, it is meant that a frame of reference and measurable coordinates can be so chosen that the values of the positions in Classes C and B are equal to the hypothetical coordinates of the points P and Q respectively, while those of Class A are equal to the coordinates of the hypothetical surface or surfaces separating P from Q.

The important proposition is here involved that all positions lie on hypothetical surfaces, while no occupied point corresponds to a position: positions do not form a continuum and are certainly not three-dimensional. It is therefore a matter of some difficulty to describe concisely the correlation between the physical point of which the position is measured and the hypothetical point which it is sometimes said to occupy, and to state accurately in terms of hypothetical points the important relation between contiguous physical points. It is important to realize that there is a difficulty and that the matter is not quite so simple as it appears at first sight; but it can be overcome. And when it is overcome, we can proceed to inquire whether the theory is true and predicts and explains true laws. The answer is (or was) that it is true, and that it predicts the laws of experimental geometry; further, it explains them in so far as the conception of a rigid body, always occupying mathematically similar regions, is acceptable and inherent in the fundamental ideas of the theory.

Further, as with all valuable theories, slight additions to the hypothesis and dictionary enable the theory to explain laws other than those on which (as we are supposing) it was originally based. By modifying slightly the idea of occupation, as defined by the dictionary, so as to permit occupation by incompressible fluids as well as by rigid bodies, we can explain the very important law relating the volume of a rigid

body, measured as a fundamental magnitude by means of Archimedes' laws, to the form of its surface. Again, by associating constants with the hypothetical points occupied by a body, these constants being properties of that body, we can explain the laws which involve (in our usual language) the interior of a body; the law of density, for example, or the laws of thermal or electrical conduction. It should be noticed that the proposition that these hypothetical constants are properties of the occupying bodies and not of the region which they occupy is equivalent to the assertion of the homogeneity of space.

And one more step is taken when there are introduced hypothetical magnitudes, similar to these constants, associated with points that are not occupied by matter. Thereby we pass from action at a distance to action through a medium, and reach the characteristic theories of 19th century physics. Of all these theories, the theory of space is an essential part; indeed, they may be regarded as successive extensions of the theory of space.

7. My object in presenting these considerations is to draw attention to the relation of the hypothetical idea of space to the experimental facts on which it is founded, and in particular to the experimental facts of geometry. But of recent years, as we all know, the theory of space is supposed to have undergone considerable change in connexion with the principles of relativity. Although it is not immediately relevant to my main purpose, it may be well to consider briefly how some of the new doctrines are to be interpreted according to the view put forward.

The chief of these doctrines, for our purpose, are that space is not absolute, but relative, and that, in the neighbourhood of massive objects, it is not Euclidean. Whether these doctrines are necessary consequences of those parts of the theory of relativity which have received experimental confirmation is a matter beyond our present inquiry; let us assume for the moment that they are. What precisely are the alterations that they involve in the older theory?

That position is relative is not a matter of theory at all; it is involved in the meaning of position. The measurement of position requires both the use of a frame of reference and the law that all frames are equivalent according to certain laws. Again, there is nothing new in the doctrine of the homogeneity of space, which makes it impossible experimentally to identify a point except by its relations to other points on the surface of occupied regions. On the other hand, the

older theory was absolute in the sense that it required the individuality of the hypothetical points; unless the conception is admitted that the points, though experimentally indistinguishable, were individual and ideally distinguishable, it is impossible, so far as I can see, to state the hypothesis and to frame the dictionary in any intelligible manner. Many, perhaps most, theories contain some hypothetical ideas not determinable experimentally: to deny validity to such ideas is to reject all theoretical physics. The absoluteness of space, in this sense, is an essential part of the theory of space: a purely relative space, in which points have no identity, is simply not space at all—unless the practice is admitted of transferring names to new concepts which have nothing in common with those to which they were formerly attached.

It is agreed universally to-day that a hypothetical non-Euclidean space is possible. Certain definitions of Euclidean space can be changed—in particular, that defining the distance of two points in terms of their coordinates,—the others remaining unaltered; and a new scheme of definitions can be set up, self-consistent and leading to a new series of propositions differing from the old, but closely analogous to them. If we leave the dictionary unaltered, the new theory will, of course, predict correspondingly different laws; the two theories may be compared and tested by experiment. In particular, if the portion of the dictionary dealing with the occupation of space by matter is left unaltered, the theory will predict laws of experimental geometry other than the Euclidean.

But it must be remembered that, if this part of the dictionary is left unaltered, other parts must be altered. Any parts referring to rigid bodies, or to either of the three fundamental geometrical magnitudes, must be altered, because these concepts derive their validity from the Euclidean laws. If those laws are not true, there are no rigid bodies, no lengths, no angles, no areas, in the sense in which those terms are used at present in experimental science. It might be possible, by a consideration of the laws, deduced from the new theory, which would take their place, to establish new concepts corresponding to those which would have to be abandoned, and to make new entries in the dictionary involving these new concepts in place of the old. But until the experiments can actually be tried, any such proceeding would be exceedingly dangerous. Imaginary experiments are a terrible pitfall. Until they can be tried,

all guesses at the relations between "lengths" of "rigid" bodies occupying a non-Euclidean space should be regarded with the utmost suspicion.

When they are made as a result of the theory of relativity, such guesses are even more precarious; for here there seems no reason to believe that the substitution of a non-Euclidean for an Euclidean space in the hypothesis would leave any part of the dictionary unaltered. For the theory of relativity demands alterations in the dictionary; it demands not mere additions, as most previous theories have done, but the actual rejection of some entries previously accepted. But if one part of the dictionary is to be altered, what evidence is there that the remainder is to be left unchanged? The denial that the length of a straight line is the distance between the extreme hypothetical points that it occupies is no more startling than many others that we now accept. But, further, the prediction from the theory of relativity of any laws of experimental geometry can be supported only if most of the dictionary is to be left in its accustomed form. Any changes in those laws predicted by the theory are far too small to be detected by actual measurements of the fundamental magnitudes by the methods on which their definition depends; they can be predicted only on the assumption that there are other methods of measuring these magnitudes, which are equivalent to the fundamental method. But this equivalence depends on various laws deducible from the older theory of space, with the older hypothesis and the older dictionary. They will not be equivalent if other laws are substituted, deducible from a new theory with a new hypothesis but the old dictionary; if they are to remain equivalent every entry in the dictionary must be appropriately revised. But if all others are to be revised, why should that relating to the occupation of space remain totally unaltered? I conclude that, even if the theory of relativity demands a hypothetical non-Euclidean space, there is no reason to suppose that, even if experiments of infinite accuracy could be made, the laws of experimental geometry would take the corresponding non-Euclidean form or that they would not remain truly Euclidean.

CVII. *The Electronic Theory of Valency.*—Part III. *The Transmission of Chemical Affinity by Single Bonds.* By Professor T. MARTIN LOWRY, C.B.E., M.A., D.Sc., F.R.S.*

1. *Transmission of Chemical Affinity by Single Bonds and by Conjugated Systems.*

IT is now generally recognized that chemical affinity can be transmitted through chains of atoms in two different ways. In the first case, one atom exerts on another an effect which is always of the same kind, although it may diminish rapidly as the distance between the atoms increases. In the second case, alternate atoms are affected in opposite ways, in accordance with Lapworth's "Principle of Alternate Induced Polarities" †. The electronic mechanism underlying this alternation of polarities has been discussed in Part II. of this series of papers ‡. The mechanism of transmission of affinity through single bonds (Lapworth's "General Effect") has been discussed briefly in Part I., as depending on a possible displacement of the nuclei relatively to the enveloping shells of electrons. The object of the present communication is to inquire whether these two mechanisms are sufficient to explain all the facts in reference to the transmission of chemical affinity through chains of atoms, or whether there is a residue of unexplained observations which demand yet another mechanism to account for them. The invention of a third mechanism would probably not present any great difficulty; but very clear proof of the real existence of an "unexplained residue" of facts must be forthcoming before the necessity of such an invention can be admitted. In the opinion of the writer the existence of this residue is still unproved.

2. *Are Alternate Polarities possible in Saturated Systems.*

In general, the theory of polar double-bonds does not allow of any extension of alternate polarities beyond the last double bond of a conjugated system, since "on every occasion where the sign + — is written a bond must be deleted in the conventional formulæ" (Trans. Chem. Soc. cxxiii. p. 824 (1923)). Lapworth § has, however, called

* Communicated by the Faraday Society.

† Manchester Memoirs, lxiv. No. 3 (1920).

‡ Compare Trans. Chem. Soc. cxxiii. p. 822 (1923).

§ *Ibid.* p. 4.

attention to the fact (which he had foreseen and predicted) that "hydrogen atoms in the γ -position in ethyl crotonate have properties precisely corresponding with those of the hydrogen atoms in the α -position in saturated carbonyl compounds." He interprets these results by writing the chain of atoms

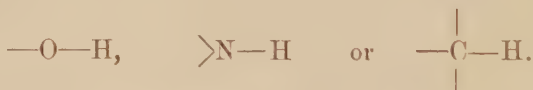


OEt

where the alternation of polarities is made to extend over two single bonds beyond the limits of the conjugated chain. In view of the ambiguous character of the valency which unites hydrogen to other atoms* the transmission of alternating polarities through one other atom to hydrogen does not present any real difficulty, since a mobile hydrogen atom can always be represented as

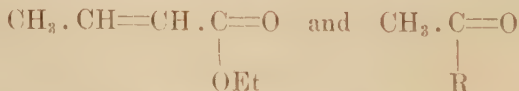


instead of



In other words, a conjugated chain may induce ionization in an adjacent group, just as ionization may induce alternate polarities in a conjugated chain, the "motive" in each case being to extend the alternate polarities over as long a series of atoms as possible.

In actual fact, Lapworth's comparison of the systems

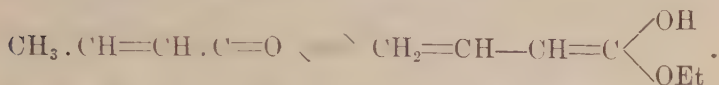


goes no further than a statement that the influence of a $>\text{C}=\text{O}$ group can be transmitted through a $>\text{C}=\text{C}<$ group to a methyl-group on the other side. This conception is entirely in harmony with the properties which have been attributed to polar double bonds in conjugated systems, and no new mechanism is necessary to explain it. It may, however, be suggested that, just as the reactivity of the ethyl groups in acetone appears to depend on a preliminary enolization†, so the reactivity of the methyl group in ethyl

* 'Chemistry and Industry,' xlii. p. 43 (Jan. 19, 1923).

† Lapworth, Trans. Chem. Soc.

crotonate may depend on an enolization which, according to the principles of Thiele, should affect the terminal groups of the conjugated chain thus :



A real test of the extension of alternate polarities to single bonds must obviously be made on atoms at such a distance from the conjugated chain (*e. g.* in a δ -position) as to be exempt from the possibility of changes such as the one set out in the preceding equation ; no such test appears to have been described hitherto.

3. Strong and Weak Bonds in Saturated Compounds.

Somewhat similar conclusions as to alternation in chains of single bonds have been reached from another point of view by Flürscheim*, who adopts the view of Claus† that “the force with which two atoms are linked is not a constant, but that, depending on the nature of the other atoms in the molecule, it must be assumed to vary from compound to compound.” The strengthening of one bond is supposed to weaken the next, and conversely ; a single unsaturated atom is therefore able to develop alternate strong and weak bonds throughout a chain of atoms, and this effect is not limited to conjugated chains, but may also occur in chains that are otherwise completely saturated. There would be no difficulty in expressing this view in terms of the electronic theory‡ ; but a critical review of the experimental facts is needed before the necessity for the introduction of an additional mechanism can be accepted.

4. Dissociation-Constants of Halogenated Fatty Acids.

Table I. shows the dissociation-constants of a series of halogenated acids at 25°. It will be seen that the influence of the halogen falls off rapidly as it is moved from an α - to a δ -position, where its effect practically disappears. In this case at least there is no slightest sign of alternation. This would, I think, be explained by Flürscheim on the ground that the halogens are strongly polar but not strongly unsaturated.

* Trans. Chem. Soc. xcv. p. 718 (1919).

† Ber. xiv. p. 432 (1881).

‡ Compare Kermack and Robinson, Trans. Chem. Soc. cxxi. p. 431 (1922).

TABLE I.

Dissociation-Constants ($\times 10^5$) of Halogenated Acids at 25°.

	$\alpha.$			$\beta.$			$\gamma.$			$\delta.$		No Halogen.
	Cl	Br	I	Cl	Br	I	Cl	Br	I	Cl	Br	
Acetic	155	156	75	1.8
Propionic.....	147	108	...	8.6	9.8	9.0	1.4
Butyric	139	106	...	8.9	3.0	2.6	2.3	1.5
Valeric.....	1.9	1.7	1.6

CH₃.CO₂H 1.8 ; CH₂Cl.CO₂H 155; CHCl₂.CO₂H 5000
 CCl₃.CO₂H 30,000; CH₂Br.CHB₂.CO₂H 670; CH₃.CBr₂.CO₂H 3300.

5. Dissociation-Constants of Unsaturated Acids.

Flürscheim relies for part of his evidence on the unsaturated acids. The data for these are set out in Table II. (a), where the dissociation-constants of the $\beta\gamma$ unsaturated acids are seen to be higher than those of the $\alpha\beta$ or $\gamma\delta$ acids.

TABLE II.

(a) Unsaturated Acids.					Saturated Acids.		
	$\alpha\beta.$	$\beta\gamma.$	$\gamma\delta.$	$\delta\epsilon.$			
C ₂ H ₃ .COOH	5.60	H.CO ₂ H 21.4	C ₂ H ₅ .COOH 1.43	
C ₃ H ₅ .COOH	2.0	CH ₃ .COOH 1.8	C ₃ H ₇ .COOH 1.5	
	3.6	3.8			
	(iso.)						
C ₄ H ₇ .COOH	1.48	3.35	2.09	...	C ₂ H ₅ .COOH 1.4	C ₄ H ₉ .COOH 1.6	
α Me	1.1	3.0	2.16	...			
β Me	0.73	2.88			
α Et	2.05	3.39			
C ₅ H ₉ .COOH	1.89	2.64	1.74	1.91	C ₃ H ₇ .COOH 1.5	C ₅ H ₁₁ .COOH 1.45	
(b) Saturated Acid. Vinyl-derivative. Chloro-derivative.							
Formic acid	21.4	5.60	Not known.				
Acetic acid	1.8	3.8	155				
Propionic acid	1.4	2.09	88.6				
Butyric acid	1.5	1.91	3.0				
Valeric acid	1.6	...	1.9 (Br)				
(c) Formic Acid.				Acrylic Acid.			
H.CO ₂ H	21.4	H.C ₂ H ₂ .COOH	5.6				
CH ₃ .COOH	1.8	CH ₃ .C ₂ H ₂ .COOH	2.0 or 3.6				
			cis? trans?				
C ₂ H ₅ .COOH	1.4	C ₂ H ₅ .C ₂ H ₂ .COOH	1.48				
C ₃ H ₇ .COOH	1.5	C ₃ H ₇ .C ₂ H ₂ .COOH	1.89				
C ₄ H ₉ .COOH	1.6						

Two alternative ways of regarding these acids may, however, be submitted. Thus in Table II. (b) the saturated

acids of the series $H.C_nH_{2n}.CO_2H$ are compared with their vinyl derivatives, $CH_2:CH.C_nH_{2n}.CO_2H$, in order to bring out the effect of the unsaturated vinyl group as a substituent. This table shows that, except in the case of formic acid, the vinyl group increases the acidity of the compound, although less strongly than a halogen, but without showing any signs whatever of alternation. In Table II. (c) the corresponding derivatives of formic acid, $R.CO_2H$, and of acrylic acid, $R.CH:CH.CO_2H$, are compared. This table shows in a remarkable way that, in both series of compounds, the diminution of acidity by the chain of carbon atoms is most marked at the ethyl-derivative, where the dissociation-constant passes through a minimum in each case. The table therefore suggests that the effect of the growing chain is handed on through the $-CH=CH-$ group to the carboxyl-group, but by a mechanism in which the two unsaturated carbon atoms act as excellent transmitters, but do not themselves count as a part of the chain*. The only way in which any alternation of properties can be detected in this series of acids is by tracing out the effect of moving the double bond along the chain. Even then the alternations are only of the same order of magnitude as those produced by *cis-trans* isomerism, *e. g.* in crotonic acid. It is therefore quite possible that these small fluctuations are steric in origin, depending on some question of the configuration of the chain, rather than on a reversal of polarity in alternate atoms.

6. Acylous and Basylous Groups.

It is usual to describe radicles which increase the strength of an acid as negative, whilst those which decrease acidity are called positive. Lapworth † regards these as misnomers, since when acetamide is hydrolysed the "positive" >NH_2 attracts the positive hydrogen ion, whilst the "negative" $-\text{CO}.CH_3$ attracts the negative hydroxyl. A similar contradiction in terms is implied in describing chlorine as a "negative" radicle because it repels a positive hydrogen ion in hydrogen chloride. Lapworth therefore proposes to use the terms "acylous" and "basylous" instead of "negative" and "positive." These terms are, however, merely relative, since they describe the change produced on introducing one radicle in the place of another. The displaced radicle

* This is also in harmony with Lapworth's observation on ethyl crotonate.

† Manchester Memoirs, lxiv. No. 3, p. 2 (1920).

is usually hydrogen, and according to the common view $-\text{CH}_3$ and $-\text{NH}_2$ are positive or basylous, whilst $-\text{OH}$ and $-\text{Cl}$ are negative or acylous. This view is also open to criticism on grounds set out below.

7. *Directly-attached Hydrogen as an Acylous Group.*

The dissociation-constants of a series of saturated fatty acids are set out in Table III.

TABLE III.

Dissociation-Constants ($\times 10^5$) of Fatty Acids.

β .	α .		γ .	β .	α .		
	H . CO . OH	21.4		CH ₃ . CH ₂ . CH ₂ . CO . OH		1.5	
	CH ₃ . CO . OH	1.8		CH ₃ } CH . CH ₂ . CO . OH		1.7	
	CH ₃ . CH ₂ . CO . OH	1.4		CH ₃ } CH . CH ₂ . CO . OH		1.7	
	CH ₃ } CH . CO . OH	1.4		CH ₃ . CH ₂ } CH . CO . OH		1.7	
	CH ₃ } CH . CO . OH	1.4		CH ₃ } CH . CO . OH		1.7	
	CH ₃ } C . CO . OH	1.0		CH ₃ . CH ₂ } CH . CO . OH		1.9	
				CH ₃ . CH ₂ } CH . CO . OH		1.9	
			ϵ .	δ .	γ .	β .	α .
					CH ₃ . CH ₂ . CH ₂ . CH ₂ . CO . OH		1.6
					CH ₃ . CH ₂ . CH ₂ . CH ₂ . CH ₂ . CO . OH		1.46

There is a very big drop in acidity on passing from formic to acetic acid; but if $-\text{CH}_3$ were really a basylous group, there should be a cumulative decrease of acidity in mono-, di-, and tri-methylacetic acids, analogous to that recorded in the case of the chloroacetic acids. Actually, the replacement of $-\text{H}$ by $-\text{CH}_3$ has very little effect on the strength of acetic acid; and when the replacement takes place at a still greater distance from the carboxyl, the sign of the effect is reversed, since the dissociation-constants of the normal fatty acids pass through a minimum at propionic acid followed perhaps by a shallow maximum at *n*-valeric acid. Under these conditions it is much more reasonable to think of $-\text{CH}_3$ as a neutral radicle, at least when studying the series of fatty acids, and to regard the directly attached hydrogen atom of formic acid as definitely acylous.

8. Acylous Character of the Amino-Group.

Much confusion has arisen from the idea, which is held almost universally, that the amino-group is strongly basylous. This is incorrect, and evidence is set out below to show that, when its direct neutralizing action is eliminated, it possesses well-defined acylous properties. This view was suggested by Vörlander in 1902*, but has failed to secure the general acceptance which it deserves. Thus Flürscheim's paper was written mainly in order to account for the "anomaly" that amino-acids are sometimes stronger than the fatty acids from which they are derived. If, however, the amino-group is really acylous, this must be a perfectly normal effect, although it is commonly masked by the formation of internal salts.

TABLE IV.

Dissociation-Constants ($\times 10^5$) of Anilino-acetic Acid, etc.

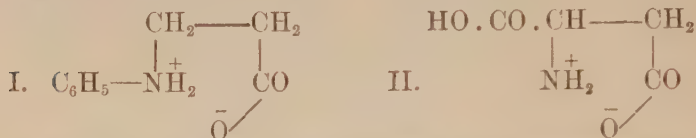
$\text{C}_6\text{H}_5 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{COOH}$	76	$\text{C}_6\text{H}_5\text{N} \begin{cases} \text{CH}_2 \cdot \text{COOH} \\ \text{CH}_2 \cdot \text{COOH} \end{cases}$	270
$\text{C}_6\text{H}_5 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{COOH}$	3.9		
$\text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$	2.3	$\text{C}_6\text{H}_5 \cdot \text{CH} \begin{cases} \text{CH}_2 \cdot \text{COOH} \\ \text{CH}_2 \cdot \text{COOH} \end{cases}$	7.7
$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$	1.4		
$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{COOH}$	1.4	$\text{CH}_2 \begin{cases} \text{CH}_2 \cdot \text{COOH} \\ \text{CH}_2 \cdot \text{COOH} \end{cases}$	4.7

Table IV., most of which is quoted from Vörlander, shows that the $-\text{NH}-$ group occupies, as might be expected, an intermediate position between $-\text{CH}_2-$, which is practically neutral, and $-\text{O}-$, which is strongly acylous. In this series of acids, the tendency of the basic amino-group to absorb the hydrogen-ions as fast as they are set free by the carboxyl, is reduced to a minimum by the influence of acylous substituents on the nitrogen. Evidence of a similar character is provided by studying the influence of the amino-group on a base where no question of neutralization can arise; the acylous character of the group is then shown by the fact that hydrazine is a weaker base than ammonia.

Exceptional behaviour may be expected when the formation of an internal salt involves the formation of a 5-atom

* *Ann.* 320. p. 99 (1902).

ring as in β -anilino-propionic acid I. or in amino-succinic acid II.



In the former case very complete neutralization occurs, and β -anilino-propionic acid (0.4×10^{-5}) is weaker than propionic acid (1.4×10^{-5}), whereas α -anilino-propionic acid (3.8×10^{-5}) is stronger; but it is the weak and not the strong acid that is the anomaly. In the latter case, amino-succinic acid is stronger than succinic acid, although α -amino-acetic acid is weaker than acetic acid. The strength of amino-succinic acid arises from the fact that the direct neutralizing action of the amino-group is fully used up by the carboxyl-group with which it forms a five-atom ring; the other carboxyl-group therefore shows the normal increase of acidity produced by an acylous substituent, undisguised by any neutralizing action.

If this view of the acylous character of the amino-group be adopted, the anomalous behaviour of the amino-acids appears to be perfectly normal and the special mechanism devised by Flürscheim to account for it is no longer needed.

10. Summary.

(a) The reactivity of the methyl-group in ethyl crotonate is in harmony with the theory of polar double bonds. It cannot be used as a proof of the existence of polarized single bonds (polar covalencies), since it receives a simple interpretation in terms of Thiele's theory of conjugation.

(b) The small fluctuations which are observed in the strength of unsaturated acids as the double bond is moved along the chain may be attributed to steric influences such as those which Pickard has discovered in optically active compounds.

(c) The fact that amino-acids are sometimes stronger than the acids from which they are derived is attributed to the acylous character of the amino-group; this is usually masked by the direct neutralizing action of the basic group.

(d) The conclusion is drawn that alternate polarities are characteristic of conjugated systems, and that it is not yet proved that they can be developed in chains of single bonds, where both acylous and basylous groups produce effects of constant sign.

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CVIII. *Notices respecting New Books.*

- (1) *Physics, the Elements.* By N. R. CAMPBELL Pp. vii+565. Cambridge University Press. 40s. net.
- (2) *Modern Electrical Theory.* Chapter xvi., Relativity. By N. R. CAMPBELL. Pp. vi+116. Cambridge University Press. 7s. 6d. net.

(1) **A**T the beginning of the first of these books it is stated that the main object is to be analysis of physics, especially with a view to ascertaining the nature of the available evidence and the meaning and reliability of the results based upon it. The need for such analysis is plain. The discussions of Mach and Pearson are good so far as they go, but they are only a beginning. A book with this object, consisting of over 500 large pages, and written by an experimental physicist with a wide knowledge of modern physical developments, might have been expected to make advances of the greatest importance in the understanding of scientific processes. There are notable contributions to the descriptions of some of these processes, but none to the understanding of scientific inference and the reasons why some judgments are considered more reliable than others.

The reason for the failure is foreshadowed on p. 3. "These inquiries will be clearly the more interesting the more fundamental are the propositions and the ideas concerning which they are made . . . it will not be our object to raise doubts concerning them; it will be rather to examine why no doubts are possible Least attention of all will be required for these branches of our knowledge where opinion is still not wholly agreed; to examine in detail propositions which may yet be rejected would be waste of time." It is, however, just precisely the propositions that are in doubt that constitute the most interesting part of science; every scientific advance involves a transition from complete ignorance, through a stage of partial knowledge based on evidence becoming gradually more conclusive, to the stage of practical certainty. By limiting his discussion to the last stage, when he thinks "no doubts are possible," Dr. Campbell has excluded from consideration everything that most interests the ordinary physicist.

It is, of course, a logical commonplace that however many instances of a general proposition may have been verified, it is impossible to infer anything whatever, either with certainty or with probability, about the result of the next attempted verification, unless we have some other general proposition to guide us.

This general proposition must evidently be accepted *a priori*. Many writers have avoided the difficulty by attempting to deduce the properties of the world from general propositions alone, which they think they know *a priori*, regarding experiments as an adventitious luxury. Dr. Campbell, on the other hand, wishes to reduce everything to experiment, excluding all *a priori* postulates, and yet to be able to make inferences. This being inconsistent with logic, he is led to deny the logical proposition altogether denying that any general proposition is used in scientific method. Thus we have on p. 112, "There is no method, and it is because there is no method which can be expounded to all the world that science is a delight to those who possess the instincts which make methods unnecessary," and on p. 354, "Such laws cannot be discovered by any formal process; they can only be suggested by some considerations for which no formal rule can be laid down and then shown to be in accordance with experiment. There is no such thing as formal induction."

This obscurantist position naturally leads the author into an attack on logic and mathematics, which he wishes to make irrelevant to science. In particular, he attempts to distinguish between the number (small *n*) of a class, and the mathematical Number (capital *N*) defined as a class of classes. This arises from a misunderstanding, not a surprising one in view of Mr. Bertrand Russell's semipopular expositions. Whitehead and Russell take as fundamental the notion of the comparison of two classes, members being selected in pairs, one from each class, a class being greater than the other if it has any members left unpaired when the other is exhausted. This is precisely Dr. Campbell's definition. The notion of a class of classes is not defined by Whitehead and Russell; they give instead an interpretation of every proposition involving it, these interpretations being such that the class of classes will have the same fundamental properties as are believed to be possessed by the number of a class, and such that formal logical development from them is possible. Consequently every proposition true of number is also true of Number, and *vice versa*. In the only sense that conveys any meaning they are therefore the same thing.

Again, Dr. Campbell suggests that the mathematical notion of function does not occur in physics, since all functions can be represented by graphs or calculated by machines, both processes being purely physical. But the use of analogy with a graph or a machine is itself a logical process, so that these devices do not avoid logic; they merely lower its quality. Further, the 0·3 per cent. accuracy possible in a graph is ridiculously inadequate for the representation of the accuracy of many known physical laws; and the process of grinding out the value of $\cos x$, term by term, on a machine can hardly be considered analogous to the way a

particle moves under a force to the origin proportional to the distance.

An analytic function is defined on p. 355 as "one which has a differential coefficient at each point of the range, except possibly a finite number of separate points." The possession of a differential coefficient at points of an *area* is one of the criteria for an analytic function of a *complex* variable, but differentiability for real values does not afford any criterion; and an analytic function may have an infinite number of singularities in a finite region. This definition appears as a footnote to a paragraph the last sentence of which is equally reliable.

A scientific law could reach a stage when "no doubts are possible" only if the *a priori* general propositions dealt with certainty and not with probability. I do not believe that they deal with certainty, for if they did there should be a stage in one's knowledge about a law when it passes suddenly from complete ignorance to complete certainty, which does not appear to be the case; and on the basis of probability inference it seems possible to establish laws with probabilities as great as are required for any ordinary scientific purpose. Dr. Campbell is, however, dissatisfied with probability inference, and wishes to attain certainty. Thus he is led into further difficulties.

He realizes the fallibility of the individual judgment, and his scheme therefore requires the substitution of something more reliable. He therefore introduces the concept of "universal agreement." Thus on p. 10 we read (A) "In science, but not in metaphysics, it is possible to obtain universal agreement for conclusions"; on p. 21 (B) "The subject matter of science may be defined as those immediate judgements concerning which universal agreement may be obtained"; on p. 216 (C) "There is a certain class of judgements concerning which universal agreement can be obtained as it can be obtained about no other class. These judgements are those about the association of sensations; not about the occurrence of sensations, but about their uniform association which determines action. These judgements if they were expressible explicitly at all would be expressed as laws, but since the ideas involved in them are more fundamental than any language they are not so expressible"; and on the same page (D) "we include only definite 'experiments' which can be repeated and can be shown to other observers." If statement C means anything it seems to contradict the use of the word 'conclusions' in A, and to imply that all persons react in just the same way to certain stimuli; and if these associations are the basis of physics these stimuli must include the spatial and temporal coincidences that physics deals with. The falseness of this statement is a commonplace of experimental psychology; the differences of the reactions of different persons to just these stimuli constitute the

subject matter of an elaborate science. Indeed they are unpleasantly familiar to all observational astronomers.

Even, however, if investigation had shown that judgments of some class were the objects of universal agreement, it would be impossible to utilize this knowledge with regard to a particular observation without the minor premiss that the particular proposition considered is an instance of the class which is a judgment possible only to the observer. The ultimate recourse to the fallible individual judgment is unavoidable.

Chapter VII. deals with probability, the Venn definition, concerning which enough has been said already, being adopted.

The establishment of any physical law is reduced to the pursuit of a further Snark. A law (p. 213) leaves the residuals in a random distribution. But they could not conceivably be distributed exactly at random unless they were infinite in number. Thus no law could ever be established at all, much less with the certainty Dr. Campbell demands. Incidentally the above test for a law makes errors methodologically prior to laws, and therefore they should have been discussed before them; actually they are considered three chapters later.

As a matter of fact the difficulty of reading the book is much increased by the author's habit of suddenly breaking off discussion of a point with a promise to return to it later, but with no indication of the place, if any, where he does return to it.

It must not be inferred from the above criticisms that the book is worthless. Chapters VIII. to XV. are for the most part very good, though they are often marred by errors arising out of those just pointed out. They deal with The Meaning of Science, Science and Philosophy, Fundamental Measurement, Physical Number, Fractional and Negative Magnitudes, Numerical Laws and Derived Magnitudes, Units and Dimensions, and the Uses of Dimensions. The notions of Fundamental and Derived Magnitudes probably constitute one of the chief advances in the subject yet made, and the discussion of dimensions is extremely illuminating. To attempt to discuss them here would, however, be useless. The book should be read.

Dr. Campbell's book must be regarded as pioneer work in an extremely difficult subject, and the best purpose such work can serve is to open up new fields for investigation. To stimulate thought is the first need; and it is impossible to read much of the book without receiving such stimulus. Most of the questions asked in this book are of the first importance; many of them are answered wrongly, but the great need of a new subject is to have the important questions asked; it is premature to hope for correct answers to all at the first attempt. When all the questions raised by Dr. Campbell have been answered, the theory of scientific method will be a well-developed science.

(2) Of the making of books on relativity there is no end. But the associated weariness of the flesh is less in this case than in most others. It is definitely addressed to those interested in relativity because it predicts something experimentally true; it is a book on physics and not on mathematics or philosophy. The author on the whole fulfils his object well. It is the most physical book on the subject yet published; completeness of argument has been sacrificed by the omission of many steps of algebra and calculus, but the reader can obtain these by referring to other works, Cunningham's 'Relativity and the Electron Theory' being the most likely to harmonize with Dr. Campbell's. Its chief purpose is to clear up the difficulties that physicists have experienced in dealing with the more mathematical expositions.

The special theory is derived from two principles, the first relating to the independence of laws of the motion of the observer, while the second is practically the usual $ds=ds'$. The Lorentz-Einstein transformation and the law of composition of velocities are derived from these. The Doppler effect, aberration, and the experiments of Fizeau and Michelson and Morley are then explained. The accounts of these physical experiments are the clearest I have seen (but on p. 27, $2l/c$ has been written for $2l/(c^2-v^2)^{\frac{1}{2}}$, and on p. 30, q has several times been written for v without explanation).

At this stage the geometrical interpretation of Minkowski is introduced. The four-dimensional space-time, one coordinate being always imaginary, is regarded as a pure device for making the mathematics easier, which is, I think, the correct attitude. The general theory is then derived from this; though I think Dr. Campbell exaggerates the extent to which the general theory is hypothetical. In the summary he appears to be approaching tolerance of mathematics.

On p. 104, line 12, "less" should be "longer," and two lines below, "rod" should be "red." Misprints are very few in both books.

HAROLD JEFFREYS.

CIX. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 719.]

May 2nd, 1923.—Prof. A. C. Seward, Sc.D., F.R.S., President,
in the Chair.

Prof. JOHN JOLY, D.Sc., F.R.S., F.G.S., delivered a lecture on the Bearing of some Recent Advances in Physical Science on Geology.

After referring to the discovery by the present Lord Rayleigh of the general distribution of radioactive materials and to the

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earlier but more recently developed discovery of isostasy, the Lecturer observed that, assuming that the dense layer upon which, according to the theory of isostasy, the continents float, is composed of basalt possessing the average radioactivity of basalts, it may be calculated that, if this substratum is now solid (as appears from both tidal and seismological evidence), it will have acquired sufficient radioactive heat to become fluid in about 30 million years.

The change of density then occurring will cause a downward motion of the continents relative to the ocean, and transgressional seas will result. After a long period, during which the liquid magma (under tidal forces) circulates from beneath the continents (which, owing to their own radioactivity, act as an adiatherminous covering) to suboceanic regions, the accumulated heat is given up to the ocean. Re-solidification of the magma ensues, and the restoration of the former higher density causes the continents to rise relatively to the oceans, and brings about the retreat of transgressional seas. In this manner, the complete cycle of a revolution finds explanation.

Mountain-building forces arising during the climax of revolution originate from two sources:—(a) the effects of the horizontal tide-generating force and of precessional force which, although probably considerable, have not yet been evaluated; (b) the effects of the changing area of the ocean-floor attending the expansion and contraction of the basaltic layer, whereby the oceanic area becomes alternately increased and diminished. Upon shrinkage the enlarged ocean-floor bears against the continents. Hence 'the highest mountains confront the widest oceans.'

Mountain-building is due much more to vertical than to horizontal forces. The mountains are not pushed up by lateral forces: these forces act upon the subsiding geosyncline to produce deformation of the semi-plastic materials. The mountains are elevated long after by the isostatic forces, the energy being traceable to the stored radioactive heat of prior ages.

Inter-revolutionary events consist of 'preparatory' disturbances, due to local increase of liquefaction of the magma: also of 'sequential' disturbances, due to relief of strain accumulated during revolution, and to the restoration of isostatic equilibrium.

The conditions now prevailing beneath the continents preclude the establishment of a steady state (that is, of thermal equilibrium), and in the past always must have done so.

The cyclical events outlined in the theory here adduced appear to be inevitable as a consequence of radioactivity and isostasy. Cyclical disturbances alone can explain the past history of the Earth's surface.